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FIELD EVALUATION OF HAZARDOUS WASTE PRETREATMENT AS AN AIR POLLUTION CONTROL TECHNIQUE

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Three commonly practiced commercial treatment processes were investigated for the removal of volatile organic compounds (VOCs) from hazardous waste: thin-film evaporation, steam stripping and fractional distillation. The data collected included limitations of the treatment technology, the VOC removal effectiveness, the characteristics of residuals and cost information. Three thin-film evaporators were evaluated, each treating different types of wastes. There was a large variation in the amount of highly volatile compounds removed by this technique, depending upon the boiling temperature of the waste stream. Four waste streams were treated in a batch steam stripper. Over 90% VOC removal was obtained in all four cases. Two aqueous/organic waste streams were treated using fractional distillation and over 90% VOC removal was obtained in both cases.

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and public health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs, and regulations of the Environmental Protection Agency, the permitting and other responsibilities of State and local governments and the needs of both large and small businesses in handling their wastes responsibly and economically.

This report presents the results of field assessments of three waste treatment techniques that have the potential for use in control of emissions of volatile organic compounds from hazardous waste facilities by removing those compounds from the waste streams. Those treatment techniques are thin-film evaporation, steam stripping, and fractional distillation. The report is intended for use by government agencies which are considering ways to reduce emissions from hazardous waste facilities and by facility operators and managers who wish to do the same. For additional information, please contact the Alternative Technologies Division of the Hazardous Waste Engineering Research Laboratory.

William A. Cawley, Acting Director
Hazardous Waste Engineering Research Laboratory

ABSTRACT

Three commonly practiced commercial treatment processes were investigated for the removal of volatile organic compounds (VOCs) from hazardous waste: thin-film evaporators, steam stripping, and distillation. The data collected included limitations of the treatment technology, the VOC removal effectiveness, the characteristics of residuals, and cost information.

Thin-film evaporators are effective for separating liquids from dissolved solids and suspended solids. Of the three thin-film evaporators evaluated, vent emissions of volatile organic compounds were observed for high-temperature vacuum operation. For atmospheric operation, there was no measurable flow. When both volatile and semivolatile wastes were processed in the thin-film evaporators, the concentrations of volatiles in the residue from the treatment process were reduced by 90 percent; however, when primarily volatiles were treated, the concentrations of volatiles in the residue were not significantly reduced.

Steam stripping and distillation of six different wastes were evaluated; sludges are more difficult to treat in these processes than in thin-film evaporation processes, but lower VOC concentrations could be obtained in the process residues. Concentrations of individual VOCs were measured as the treatment process continued, and the rate of removal of the VOCs was generally proportional to the concentration present. The main air emissions source identified for these processes was the condenser vent, with rates of 0.0029 and 0.0035 g/sec measured for two steam stripping batches. The air emission rates from the first distillation batch were variable, with a typical value of 0.06 g/sec. The air emissions from both the condenser vent and the receiver vent of the other distillation batch were less than 0.002 g/sec.

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SECTION 1

INTRODUCTION

BACKGROUND

The EPA Office of Air Quality Planning Standards (OAQPS) is developing regulations under the 1976 Resource Conservation and Recovery Act (RCRA) and its 1984 amendments to control air emissions from hazardous waste treatment, storage, and disposal facilities (TSDF). The purpose of the air emissions regulations is to protect human health and the environment from emissions of volatile compounds and particulates.

The sources of TSDF emissions include storage tanks, treatment processes, surface lagoons, landfills, land treatment, and drum storage and handling facilities. There are approximately 5,000 TSDF locations in the United States where one or more of these activities are in progress. The majority of sites are part of industrial facilities, while the rest are commercial facilities that accept wastes from offsite.

Research has concentrated upon the characterization of uncontrolled emissions from these sources through field measurements and by determining the reliability of emissions models. Recent investigations have identified a number of options for controlling volatile air emissions from TSDFs. These include restricting the VOC concentrations of wastes going to sources where volatile air emission rates would be high, the "pretreatment" of wastes to remove volatiles, and the use of in-situ (i.e., add-on) control techniques at the TSDF. In addition, changes in waste management practices (such as holding tanks instead of ponds) may be a cost-effective control option.

Pretreatment is a viable volatile air emissions control option and is in current use at several TSDFs. In general, it is attractive because it can be used by either the waste generator or the TSDF operator to remove volatiles from the waste before there is much opportunity for air emissions to occur. Pretreatment may be a cost-effective control technique for TSDF emissions sources with large surface areas, such as land treatment facilities and lagoons. In disposal surface impoundments (e.g., evaporation ponds) and aeration tanks and lagoons, pretreatment appears to be an important option because these TSDF processes rely on transfer of water or oxygen between the waste and the atmosphere as part of the disposal or treatment process, making process covers unattractive.

PURPOSE OF THE PROGRAM

The purpose of this investigation was to collect data for the support of regulations which consider waste pretreatment as an alternative for the control of volatile air emissions from TSDFs. To the extent possible, these data were collected from the TSDFs that are treating hazardous wastes or from the treatment of similar wastes at other industrial/commercial operations in order to permit a comparison of pretreatment to other emission controls.

Field data on several waste treatment techniques were collected to determine (1) how efficiently they remove volatiles from hazardous waste streams, (2) what the removal costs are, (3) how the byproducts from the pretreatment technologies are collected and disposed, and (4) what limitations (in terms of waste types, volatile concentrations, etc.) are placed on the use of such treatment techniques. These data documented the viability for treating specific waste streams by specific treatment techniques. Data from treatment equipment manufacturers and engineering judgment were then used to analyze the applicability of each technique to treat other waste streams and to determine technology capital, overhead, and management costs.

PROCEDURES

For the processes selected for evaluation, field data were collected at representative sites for thin-film evaporation (3 sites, 3 batches), direct injection steam stripping, (1 site, 4 batches), and distillation (1 site, 2 batches). Telephone interviews were held with a number of facilities before sites were selected for 1-day visits. On that first visit, the operating practices were discussed with the plant management, and information on process limitations, process operating conditions, equipment costs, and other factors was collected.

On the first visit, grab samples were taken while following QA/QC procedures, and the samples were analyzed in the laboratory. Relevant process measurements such as velocities, flow rates, and temperatures were recorded or measured. These data were analyzed to determine process effectiveness, and the potential for air emissions (in the case of the three thin-film evaporators) was investigated during the 1-day visit.

Field tests were planned for the processes of steam stripping and distillation. These tests sampled batches of waste as they were being treated to determine, on a compound-specific basis, the rates of VOC removal as a function of time. Thin-film evaporators were generally being used to treat waste streams with an organic content above 30 percent, and removal of lower concentrations of VOCs from waste (as could be achieved with steam stripping and distillation) was of primary concern. In addition to monitoring the concentration in the batch of waste being treated, attempts were made to monitor the flow rates of all process streams: steam, product, reflux, vent releases, and others. In some cases, it was not possible to perform the desired measurements; in these cases, the value was estimated or calculated on the basis of other measurements.

For air emissions, two techniques were available to measure concentrations: carbon adsorption tubes and evacuated steel containers. The steel containers were used for the planned field tests since the carbon tubes had a limited retention of chlorinated low-molecular-weight VOCs in the presence of water vapor. The velocity of air streams was measured with an Alnor velometer, as were wind velocities. In some cases, a dry gas meter could be used to measure flow rates of vent emissions.

Liquid samples were taken in 40 mL VOC bottles; both the headspace concentration and the liquid concentration of individual VOCs were measured by gas chromatography (GC). For some solidified samples, the headspace concentration was the only measurement of VOCs that was made. The compound identification by retention time in the GC analysis was verified by a nonquantitative GC/mass spectroscopy procedure.

The concentration data was analyzed by calculating the partition coefficient for the compounds in the waste and headspace phases. These values were compared to the partition coefficients calculated from the process data. First-order decay equations were used to correlate the removal rates of VOCs from the waste being treated.

SCOPE OF THE REPORT

This report documents the use and effectiveness of pretreatment as a method of controlling volatile emissions at TSDFs. The types of pretreatment options considered include thin-film evaporation, steam stripping, and distillation. The types of waste streams that were considered are those of significant volume which potentially emit hazardous emissions from (1) land treatment; (2) aeration tanks and lagoons; and (3) treatment, storage, or disposal surface impoundments. RTI and its subcontractors, Associated Technologies, Inc. (ATI) and Industrial Environmental Analysts, Inc. (IEA), performed the sampling and analyses and the engineering evaluation.

The major conclusions of the report are summarized in Section 2. These include comparisons of the cost-effectiveness of thin-film evaporation, steam stripping, and distillation as VOC removal techniques. Conclusions about the amount of residuals produced by each individual process and the process limitations for use to treat hazardous waste area also provided. A discussion of the sources of volatile organic compounds (VOCs) is presented in Section 3. Section 4 presents a discussion of why the three treatment technologies were chosen for study. Sections 5 and 6 provide general engineering descriptions of thin-film evaporation and distillation, respectively. These are intended to indicate how the processes operate, what types of wastes they can treat, and, in general terms, what their technical limitations are. For similar discussions of steam stripping, a recent EPA report entitled "Process Design Manual for Stripping of Organics" (EPA, 1984) should be referenced.

Section 7 reports findings from 1-day site visits to three facilities operating thin-film evaporators. Limited sampling and analysis conducted during these visits on process influent and effluent streams are reported. In Section 8, the results of a 3-day field assessment of a batch steam stripper at a TSDF are reported. A similar field assessment of two fractional distillation units at another TSDF is reported in Section 9. Section 10 summarizes the findings from the previous site visits and field studies and presents analyses of the data to make comparisons between the three types of treatment processes with respect to their suitability for VOC removal from hazardous wastes.

The appendixes to the report present the analytical results (Appendix A), process data for the field tests for steam stripping (Appendix B, the analytical procedures (Appendix C), and quality assurance (Appendix D). Appendix E presents the methodology used in estimating the cost-effectiveness of steam stripping, and Appendix F contains selected sample calculations.

SECTION 2

CONCLUSIONS

GENERAL CONCLUSIONS

1. Waste treatment is not being practiced for the purpose of VOC control.

2. Based upon information obtained from field visits including operator comments and EPA sampling and analysis, Table 1 presents potential uses of three treatment techniques for VOC removal. All three techniques are applicable to aqueous, as well as organic and mixed aqueous/organic streams. However, their applicability is limited by other waste characteristics shown in the table.

TABLE 1. LIMITATION OF TECHNOLOGIES DUE TO SELECTED WASTE CHARACTERISTICS

Waste characteristics	Thin-film evaporation	Batch steam stripping	Distillation
Over 95% water content	A	A*	A*
Polymerizable waste	P	P	P
Presence of dissolved solids	A	A*	P*
Waste containing sludges and tars	A*	P	N
Highly viscous waste	N	N	N

A	Applicable technique
P	Potentially applicable
N	Not applicable

*Waste/treatment combinations for which field sampling and analysis was performed as documented in this report.

3. The cost of waste treatment is sensitive to the concentration of VOC in the influent waste. For a fixed percent of VOC removal, costs rise as the initial VOC concentration decreases. For many wastes, the value of the recovered VOCs is less than the treatment costs.

4. Treatment of aqueous waste streams for VOC removal can significantly decrease their disposal cost by making them amenable to discharge to municipal sewers.

THIN-FILM EVAPORATORS

1. Thin-film evaporators permit the recovery of VOCs from waste materials containing sludges and tars. Typically greater than 80 percent organic recovery is achieved. Thin-film evaporators may not adequately process wastes that are reactive (polymerization) or that contain large pieces of solid material. VOC removal efficiencies in the residual waste material were 23 to 99.9 percent.*

2. The overhead product from the thin-film evaporator can be treated by distillation, carbon adsorption, and other separation or reaction processes applicable to liquids.

3. The major air emission source from a thin-film evaporator is the vacuum vent. Under abnormal operating conditions (e.g., inadequate condenser cooling), the emissions could be significant. Under normal operations, emissions are expected to be much less than VOCs recovered.

4. Since some liquid must remain in the product bottoms to maintain waste viscosity, VOC concentations will remain relatively high in some wastes treated by thin-film evaporation. The VOCs can be selectively removed from high boiling liquids. However, if the waste is a mixture of low boiling compounds, significant amounts of these compounds remain in the bottoms. This suggests that the emissions (g VOC/liter waste) will not be significantly lower for the treated waste than for the untreated waste, although waste volumes will be reduced.

5. Costs of waste treatment using thin-film evaporation ranged from $0.033 to $0.37/L of VOC recovered.

STEAM STRIPPING CONCLUSIONS

1. Steam stripping is effective for reducing the concentration of VOCs to levels of 0.1 percent or lower. Removal efficiencies of 99 to 99.8 percent were observed.

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*All processes tested were at recycling firms and the extent of waste stream treatment was determined by economic considerations, not technical constraints. Therefore, VOC removal efficiencies reported here are lower limits for the combinations of processes and waste streams tested.

2. The amount of steam required to remove the VOCs in waste materials is greater than predicted from equilibrium partitioning based on vapor pressure and solubility in dilute aqueous solutions.

3. The rate of volatile removal was logarithmic in nature, with substantially longer times required to remove the VOCs at lower concentrations than at higher concentrations.

4. The air emissions from the steam stripping process tested are much lower than the amount of VOCs recovered from the waste.

5. Costs of treatment ranged from $0.17 to $0.53/L VOC recovered for streams that are typically recycled at the facility visited, but were as high as $4.34/L for streams of low (<10 percent) VOC concentration.

DISTILLATION CONCLUSIONS

1. The individual VOC components can be removed from the waste material by batch distillation. Removal efficiencies of 99 percent and greater were observed, with resultant VOC concentrations below 0.1 percent.

2. The removal rates of the components are a function of the waste matrix and the ratio of the rate of steam to the batch size, and they are generally proportional to the VOC concentration in the waste. In the distillation process with reflux to the column, the more volatile materials were selectively removed first from the waste.

3. In the two processes tested, air emissions from the process vents represented only a relatively small fraction (less than 0.2 percent) of the VOC present.

4. Costs of treatment were typically in the range of $0.20 to $0.70/L of VOC recovered, but were estimated to be as high as $1.18/L for streams of low (<10 percent) VOC concentration.

SECTION 3

TSDF AIR EMISSIONS SOURCES

This section discusses the air emissions sources at TSDFs. The number of TSDFs, the volume of the waste streams, and the major sources of air emissions are discussed. This overview describes the context in which pretreatment may be applied to reduce VOC emissions from TSDF processes.

TYPES OF SOURCES

Hazardous waste treatment, storage, and disposal facilities contain a number of potential sources of air emissions of volatile organic compounds (VOCs). Treatment sources of VOC emissions include process tanks, cooling towers, aerated lagoons, and process leaks. Storage emissions include VOC fugitive losses from lagoons, leaking drums, and tanks. Ultimate disposal VOC emissions result from operations such as land treatment, surface impoundments, and landfills. Processes such as surface impoundments are expected to release a substantial amount of the VOC originally present in the waste, whereas only a small fraction of the VOC is expected to produce air emissions from storage leaks. Many potential emission points exist in the lifecycle of waste, from the point of generation to ultimate disposal. One advantage of pretreatment is that it can be used at the point of generation to control VOC emissions for all subsequent waste management operations.

Table 2 presents the total quantities of waste materials treated, the average quantities treated, and the number of facilities treating hazardous waste by each treatment process type employed at TSDFs. Much of the treatment was in tanks and surface impoundments which can be significant sources of TSDF emissions.

Table 3 presents the total quantities stored, average quantities stored, and the number of facilities storing hazardous waste by storage process type. Again, surface impoundments constituted the major process type. The disposal quantities, the average quantity disposed, and the number of facilities disposing of hazardous waste by each disposal process type is presented in Table 4. Surface impoundments and injection wells are the major disposal method.

Relatively large numbers of facilities handled organic wastes, solvent wastes, and nonhalogenated solid wastes (Dietz, 1984). Many of the facilities either incinerate or deep-well inject the waste streams containing volatile organic compounds; however, in many other cases, the waste streams containing VOCs are treated in treatment tanks, stored in surface impoundments, and placed in landfills and land treatment facilities, all of which can be significant sources of emissions.

TABLE 2. 1981 TOTAL ANNUAL QUANTITIES TREATED, AVERAGE ANNUAL QUANTITITES TREATED AND NUMBER OF FACILITIES TREATING HAZARDOUS WASTE BY EACH TREATMENT PROCESS TYPE (Dietz, 1984)

Treatment Process Type	Total Quantity Treated By Process Type		Average Quantity Treated Per Plant by Process Type		Number of Facilities Treating By Each Process Type
	(Billion Gallons)	(1,000 Metric Tonnes)	(Million Gallons)	(Metric Tonnes)	
Treatment Tanks	8.73	32	14.3	53	609
Treatment Surface Impoundments	16.60	62	40.6	151	410
Incinerators	0.45	1.7	1.9	7	240
Other Treatment	4.58[a]	17[a]	12.9[a]	48[a]	392[b]

[a] Based on 355 facilities that were not in combination with the above processes.

[b] Includes 37 facilities that were in combination with the above processes.

TABLE 3. 1981 TOTAL ANNUAL QUANTITIES STORED, AVERAGE ANNUAL QUANTITIES STORED AND NUMBER OF FACILITIES STORING HAZARDOUS WASTE BY STORAGE PROCESS TYPE (Dietz, 1984)

Treatment Process Type	Total Quantity Treated By Process Type		Average Quantity Treated Per Plant by Process Type		Number of Facilities Treating By Each Process Type
	(Billion Gallons)	(1,000 Metric Tonnes)	(Million Gallons)	(Metric Tonnes)	
Storage Tanks	5.10	19,300	3.57	13,500	1,428
Storage Containers	0.16	600	0.045	170	3,577
Storage Surface Impoundments	14.10	53,400	25.6	96,900	552
Waste Piles	0.39	1,500	2.2	8,300	174
Other Storage	0.26[a]	980[a]	1.9	7,200	139[b]

[a] Based on 355 facilities that were not in combination with the above processes.

[b] Includes 37 facilities that were in combination with the above processes.

TABLE 4. 1981 TOTAL ANNUAL QUANTITIES DISPOSED, AVERAGE ANNUAL QUANTITIES DISPOSED AND NUMBER OF FACILITIES DISPOSING OF HAZARDOUS WASTE BY EACH DISPOSAL PROCESS TYPE (Dietz, 1984)

Treatment Process Type	Total Quantity Treated By Process Type (Billion Gallons)	Total Quantity Treated By Process Type (1,000 Metric Tonnes)	Average Quantity Treated Per Plant by Process Type (Million Gallons)	Average Quantity Treated Per Plant by Process Type (Metric Tonnes)	Number of Facilities Treating By Each Process Type
Injection Wells	8.60	32,500	99.0	375,000	87
Landfills	0.81	3,100	4.1	15,500	199
Disposal Surface Impoundments	5.10	19,300	44.0	166,500	116
Land Application (Treatment)	0.10	400	1.4	5,300	70
Other Disposal	0.02	75	3.3	12,500	7

SIZE OF SOURCES

A few of the TSDFs are substantially greater in size than the other TSDFs. Also, most of the waste is managed in relatively few of the facilities. Table 5 presents a distribution of TSDF sizes. The distribution of TSDF sizes is approximately log normal as illustrated in Figure 1, with a standard deviation of approximately 4. Table 3 indicates that there is a large variation in facility size. Fifty percent of the TSDFs handle less than 76,000 L (20,000 gal) of hazardous waste per year, while 25 percent handle up to 10 times this much. Another 5 percent handles over 91 million L (24 million gallons) per year.

The implication of the spread of facility sizes is that the size of the pretreatment units may vary greatly from site to site. Small TSDFs would be likely to run batch treatment processes and may have a large variation in stream composition. The unit costs of treating wastes at large facilities are likely to be lower than at smaller operations because the large facilities may be able to both use continuous treatment and benefit from the economies of large-scale process equipment.

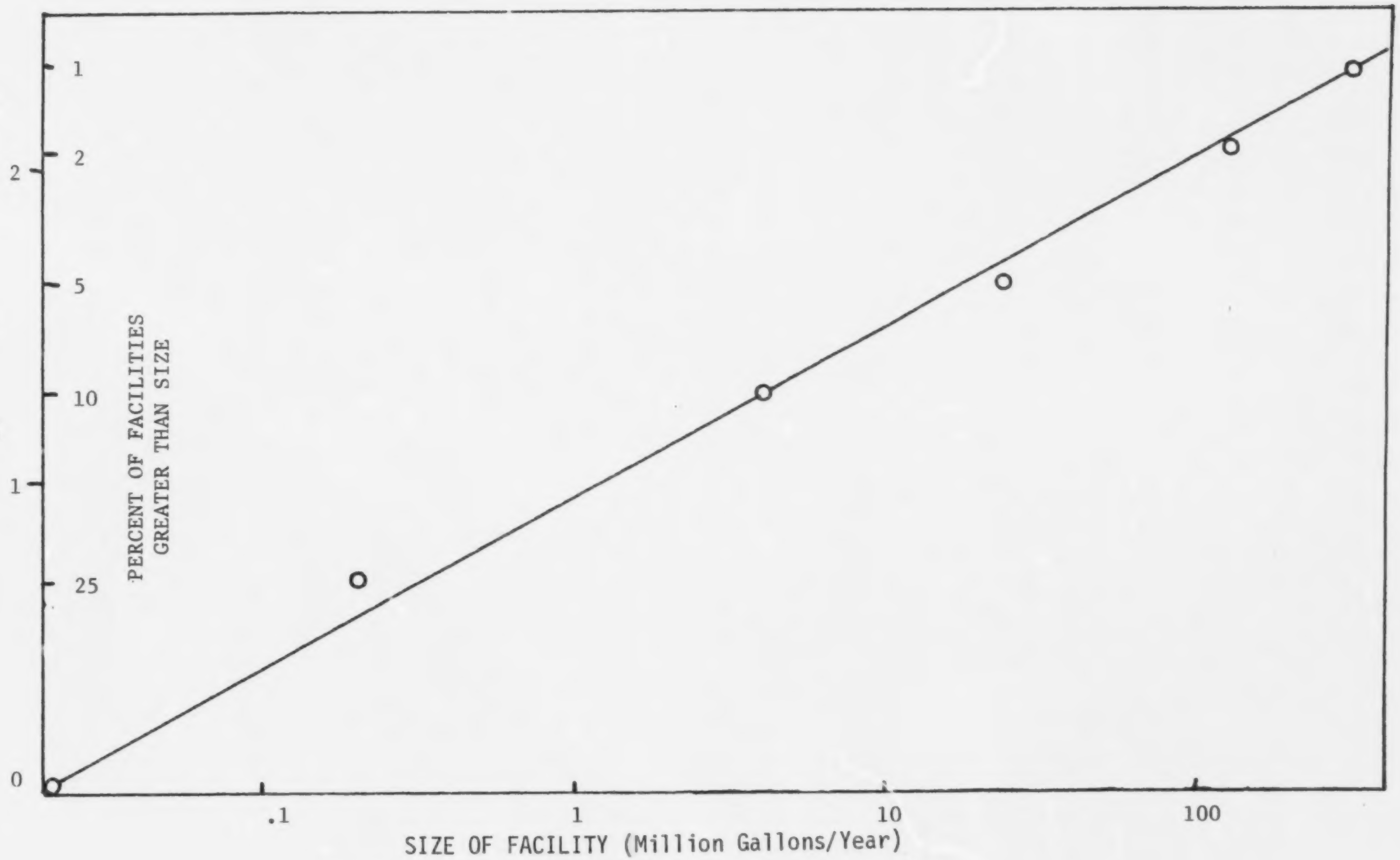

FIGURE 1. CUMULATIVE DISTRIBUTION OF TSDF SIZE
(EPA, 1984)

TABLE 5. DISTRIBUTION OF TSDF SITES

Approximate size of facility		Percent of facilities greater than size	Normal probability function F(x)
Million gal/yr	Thousand metric tonnes/yr		
306	1,200	1	2.33
130	500	2	2.05
24	91	5	1.64
4	15	10	1.28
0.2	0.8	25	0.68
0.02	0.08	50	0

SECTION 4

SELECTION OF PRETREATMENT PROCESSES AND WASTES FOR EVALUATION

The major purpose of this report is to document the performance of treatment techniques which can be used to remove volatile organic compounds from hazardous wastes. If the volatile organic compounds are removed from the wastes before the wastes are handled at a TSDF, then the emissions of volatile organic compounds would be reduced at these facilities.

On the basis of the previous RTI report entitled, "Preliminary Assessment of Hazardous Waste Pretreatment as an Air Pollution Control Technique," by James Spivey, 1984, various pretreatment techniques were identified which were potentially applicable to removing VOCs from hazardous waste. These techniques included carbon adsorption, resin adsorption, biological treatment, distillation, evaporation, chemical oxidation, wet oxidation, ozonalysis, physical separation, solvent extraction, air stripping, and steam stripping. The appropriateness of these waste treatment techniques depends upon the nature of the waste material in some cases. For example, chemical oxidation and ozonalysis are more appropriate for low concentrations of VOCs, but distillation is more appropriate for medium or high concentrations of VOCs in the waste. The processing of sludges is not practical in certain types of process equipment.

The waste streams of interest for the present study are predominantly those that are generated in large volumes and for which the treatment, storage, or disposal of these waste streams can result in significant VOC emissions to the air. These types of waste are primarily composed of mixed wastes (organics and water) and aqueous wastes.* In the selection of the waste treatment technologies which would be of most interest, techniques which were limited in the types of wastes that could be treated or techniques for which substantial information is already available (e.g., carbon adsorption) were not emphasized. Commercial techniques which were applicable to a variety of wastes were investigated because they are potentially available for immediate application to VOC control problems.

Table 6 presents the different ranges of volatility for hazardous waste components. Examples of compounds that are in each range are shown. Pretreatment techniques which rely on vapor phase mass transfer such as steam stripping, air stripping, distillation, and evaporation are much more appropriate for the volatile and semivolatile components than are the components of low volatility. Pretreatment techniques such as extraction and reaction are potentially applicable to each of the components independent of the vapor pressure.

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* For the purposes of this report, aqueous wastes are defined to contain at least 97% water and little solids.

TABLE 6. RANGES OF VOLATILITY FOR HAZARDOUS WASTE COMPONENTS

COMPONENT	VAPOR PRESSURE (mm Hg)
VOLATILE	
Benzene	95
Acrylonitrile	100
Carbon Tetrachloride	90
Methyl Ethyl Ketone	71
Toluene	88
Xylene	10
Tetrachloroethane	5
SEMIVOLATILE	
Phenol	0.34
Aniline	0.33
Toxaphene	0.3
Naphthalene	0.1
Tridecane	
LOW VOLATILITY	
Mercury	0.0018
Parathion	0.00002
PCB-1254	0.00008
Dioxin	

For the purposes of this study, it was decided to focus primarily on organic compounds which are considered volatiles based on the ability to analyze their presence in water through a purge and trap technique (Method 624). The basis for this decision was the fact that it has been found in earlier studies of emissions from TSDFs (Radian) that over 95 percent of the emissions from surface impoundments and land treatment areas were volatile compounds, while semivolatiles contributed little to emissions. While waste streams were selected for study because they contained such volatile compounds, some streams also contained semivolatiles and potential for removing them was also determined.

In the selection of waste streams which are produced in large volumes, it is important to relate the characteristics of the waste with the current practices of waste disposal. Table 7 presents a VOC pretreatment waste characterization code which the authors developed to categorize characteristics related to stream treatability. The three major waste stream characteristics which were considered for identifying appropriate pretreatment techniques were (1) the general composition of the waste (aqueous, solid, organic, or water-organic mixture), (2) the presence of tars or solids, and (3) the water solubility of the VOCs contained within the waste. Aqueous streams could be handled entirely differently than solid streams, and the presence of tars of other solids could limit applicable technology as, for example, through the contamination of activated carbon used for adsorption. As another example, the steam stripping of water soluble VOCs would not necessarily result in an effective pretreatment.

These waste codes were applied to the waste streams in an early version of the Waste-Environment Technology (WET) Model Data Base (SCS, 1983). Table 8 presents a collection of the waste streams organized by the above VOC pretreatment waste characterization code. These streams included all the streams in the SCS reference which contained VOCs (more recent versions of the data base do not contain additional disposal information and were not included). Predominantly organic streams were typically landfilled and incinerated. There is also a strong potential for waste recycling for these streams. Mixed waste streams undergo a variety of different treatment or disposal practices. In addition, there was less known about the disposal procedures for these types of waste. Aqueous wastes either were typically treated with activated carbon or were biologically oxidized.

Since the process that was used to dispose of mixed and aqueous waste streams appeared to have high potential for emissions (Table 8), and since these streams are not frequently recycled, it was decided to concentrate in this study on these two broad categories of wastes.

In order to identify the waste treatment types that should be studied in the field, a preliminary assessment of technique applicability by waste stream class was made. The organic wastes are typically subject to solvent recovery and incineration, and these were not emphasized in the present study program; however, there would be a need for treating the mixed waste and the aqueous waste, since they are often treated or disposed of in processes which have a high potential for VOC emissions (e.g., surface impoundments). Table 9 presents a selection of waste pretreatment options according to the

TABLE 7. RTI VOC PRETREATMENT WASTE CHARACTERIZATION CODE

1. First Code Letter	
S	solid, predominantly solids
O	organic, greater than 75% organics
M	mixed, aqueous soluble organics
A	aqueous, less than 3% of liquid is organics
2. Second Code Letter	
T	contains tars or high molecular weight material
S	contains solids
L	liquid stream
3. Third Code Letter	
V	contains very soluble VOCs
S	contains soluble VOCs
I	contains insoluble VOCs

TABLE 8. A COLLECTION OF WASTE STREAMS ORGANIZED BY VOC PRETREATMENT WASTE CHARACTERIZATION CODES

MAJOR ORGANIC COMPONENT (SCS, 1983)	WET STREAM NUMBER (SCS, 1983)	VOC PRETREATMENT CODE	TOTAL AMOUNT OF ORGANICS GENERATED (Kg/day) (SCS, 1983)	TREATMENT/DISPOSAL METHOD* (SCS, 1983)
Phthalic Anhydride	03.05.02	STS	1929	Landfill
Dichloropropanols	03.05.07	SSS	9920	Landfill, incineration
Naphthalene	03.05.09	SSI	64925	
Dialkylbenzene	03.05.09	SSI	64925	
Tetrachloroethane	03.05.03	SSI	49572	Landfill, incineration
Allyl alcohol	03.04.30	OTV	245	Incineration
Trichloroethane	03.04.04	OTS	151317	Landfill, incineration
Trichloroethane	03.04.05	OTS	104688	Landfill, incineration
Cyclohexanol	03.04.18	OTS	6237	Incineration
Dichloropropene	03.04.23	OTI	11925	Incineration
Chlorophenol	03.04.29	OTI	244	
Phenol	03.04.13	OSV	4134	Incineration
Butanol(s)	03.04.24	OSS	58900	Incineration
Trichloropropane	03.04.02	OSS	16704	Incineration
Trichloroethylene	03.04.03	OSI	69660	Landfill, incineration
Tetrachloroethene	03.01.04	OSI	48960	
Toluene	03.01.90	OSI	32880	
Toluene	03.02.90	OSI	8220	
Hexachlorobenzene	03.04.12	OSI	1260	Landfill, incineration
Trichloroethylene	03.02.01	OSI	63	
Methyl acetate	03.04.22	OLV	274234	
Aniline	03.04.15	OLV	4905	Landfill
Trichloroethane (1,1,1)	03.04.16	OLV	4781	Incineration
Acetaldehyde	03.04.26	OLV	3611	Incineration
Acrolein	03.04.30	OLV	245	Incineration
Benzene	03.04.21	OLS	25440	Unknown
Cyclohexane	03.04.08	OLS	3180	Incineration, landfill
Hexachlorobutadiene	03.04.11	OLI	110523	Incineration, landfill, deep well injection
Benzal chloride	03.04.01	OLI	87513	Incineration
Tetrachloroethane	03.01.05	OLI	47360	
Trichlorobenzene (1,2,4)	03.06.03	OLI	12326	
Benzene	03.04.19	OLI	6945	Incineration
Dinitrobenzene-M	03.04.09	OLI	3914	Landfill
Hexachoroethane	03.05.01	OLI	1920	Landfill, incineration
Chloroform	03.06.01	OLI	790	Landfill, incineration
Trichlorobenzene (1,2,4)	03.04.01	OLI	253	Incineration
Hexachlorobenzene	03.04.31	OLI	189	
Dimethyl alkylamine	03.04.32	OLI	66	Incineration
Toxaphene	03.04.32	OLI	66	Incineration
Cyanide	01.03.02	MSV	1929	
Trichloroethylene	03.01.06	MSI	17360	
Benzo(a)pyrene	04.02.01	MSI	1890	
Benzo(a)pyrene	04.02.02	MSI	876	
Mercury	01.01.03	MSI	404	
Mercury	01.01.02	MSI	17	
Dichloroethane (1,2)	02.02.09	MLV	136	Deep well injection, Incineration
Benzene	02.02.08	MLV	41798.4	Aerobic digestion
Acetaldehyde	03.04.14	MLV	36216	Deep well injection
Acrolein	03.04.28	MLV	1003.2	Incineration
Phenol	02.02.21	MLV	360	Unknown
Paraldehyde	02.02.06	MLV	255	Biooxidation
Methyl methacrylate	02.02.15	MLS	11484	
Ethanol	03.04.27	MLS	7936	Unknown
Acetaldehyde	02.02.12	MLS	6636	Unknown
Carbon Tetrachloride	02.02.20	MLI	1560	
Methyl ethyl ketone	02.02.22	MOV	1152	
Methyl ethyl ketone	02.02.23	MOV	148	

(Continued)

TABLE 8. (Continued)

MAJOR ORGANIC COMPONENT (SCS, 1983)	WET STREAM NUMBER (SCS, 1983)	VOC PRETREATMENT CODE	TOTAL AMOUNT OF ORGANICS GENERATED (Kg/day) (SCS, 1983)	TREATMENT/DISPOSAL METHOD* (SCS, 1983)
Toluene diisocyanate	03.05.05	ATV	3	Landfill
Benzene	02.02.13	ATS	232845	
Benzene	02.02.14	ATS	178920	
Naphthoquinone-1,4	03.05.06	ATI	5013	
Phenol	02.01.02	ASV	8160	
Cyanide	01.03.01	ASV	1666	
Acetonitrile	02.02.02	ASI	81921	
Chlordane	02.03.91	ASI	81654	
Parathion	02.03.90	ASI	81654	
Naphthalene	03.06.02	ASI	16815	
Mercury	01.01.12	ASI	1228	
Toxaphene	02.03.01	ASI	138	
Acenaphthene	02.04.01	ASI	70	
Pentachorophenol	02.01.01	ASI	35	
Ethylene oxide	02.02.17	ALV	43650	Biooxidation
Acetic acid	02.02.01	ALV	32850	Deep well injection, anaerobic lagoon, landfill
Maleic anhydride	02.02.10	ALV	8332	Biooxidation
Phenol	02.02.19	ALV	4225	Biooxidation
Benzene	02.02.04	ALV	942	
Phenol	02.01.03	ALS	91392	
Phenol	02.02.16	ALS	84000	Unknown
Aniline	02.02.11	ALS	25600	Aerobic digestion
Formaldehyde	02.02.18	ALS	5250	Biooxidation
Carbon Tetrachloride	02.02.03	ALS	2	
Toluene	02.02.07	ALI	290	Unknown
Benzene	02.02.05	ALI	3	Deep well injection, activated carbon

*The treatment/disposal method is the current treatment/disposal method identified in the reference.

TABLE 9. A PRELIMINARY SELECTION OF WASTE PRETREATMENT OPTIONS ACCORDING TO THE VOC PRETREATMENT WASTE CHARACTERIZATION CODE

Code for waste stream category	Steam stripping		Distillation column(s)		Liquid phase carbon adsorption	
	Applicable	System/ stream category	Applicable	System/ stream category	Applicable	System/ stream category
ASI	w/solid removal or TFE	S1	w/solid removal	D1	w/solid removal MW dependent	CA1
ASS	w/solid removal or TFE	S2	w/solid removal	D1	w/solid removal MW dependent	CA2
ASV	w/solid removal or TFE	S2	may need LCA add on	D2	w/solid removal MW dependent	CA2
ALI	Yes	S3	Yes	D3	MW dependent	CA3
ALS	need LCA add on	S4	Yes	D3	MW dependent	CA4
ALV	need LCA add on	S4	may need LCA add on	D4	MW dependent	CA4
ATI	w/tar removal or TFE	S5	No	--	No	--
ATS, ATS	w/tar removal or TFE	S6	No	--	No	--
MSI, MSS, MSV	w/solid removal or TFE and DC add on	S7	w/solid removal	D5	No	--
MLI, MLS, MLV	add on	S8	Yes	D6	No	--
S	No	S9	No	--	No	--

Waste Stream Categorization Code (XYZ):

X	Y	Z
Solid	Tar	Very soluble
Organic	Solids	Soluble
Aqueous	Liquids	Insoluble
Mixed		

Other abbreviations: TFE = thin film evaporation; LCA = liquid phase carbon adsorption; DC = distillation column; MW = molecular weight.

VOC-pretreatment waste characterization code. Steam stripping, distillation columns, and liquid phase carbon adsorption were considered for these streams. Nine waste categories where steam stripping was potentially applicable are identified as S1-S9. Six stream categories which would be appropriate for distillation are identified as D1-D6. Four different categories believed to be appropriate for liquid phase carbon adsorption are identified as CA1-CA4.

Because the carbon adsorption was applicable to only a limited number of streams, would require preliminary solid removal for most solid waste streams, and would not necessarily preferentially remove volatile organics, it was decided to not investigate this technology in the present study. Steam stripping and distillation were chosen for investigation because of their potential applicability to a wide range of waste categories and because they could be used to treat waste of intermediate organic content, 0.5 to 50 percent. As the study progressed, it became evident that thin-film evaporation (TFE) is most applicable for waste with high organic content and low-to-intermediate viscosity. The study also sought to find hazardous waste treatment sites using air stripping, since this technique may be less costly than steam stripping. Only one hazardous waste site was identified which uses air stripping for VOC removal from wastes, but a thorough study of the facility had not been completed at the time of the present report.

SECTION 5

REMOVAL OF VOLATILE ORGANICS FROM HAZARDOUS WASTES USING MECHANICALLY AGITATED THIN-FILM EVAPORATORS

INTRODUCTION

In the selection of potential pretreatment processes for removing volatile organics from hazardous wastes, agitated thin-film evaporation must be considered for those wastes that would foul or plug conventional evaporators. Certain slurries, sludges or viscous wastes which cannot be handled by flash evaporators, forced circulation evaporators, distillation columns, falling film evaporators or other conventional equipment can be successfully processed in agitated thin-film evaporators.

EQUIPMENT DESIGN

Agitated thin-film evaporators are designed to spread a thin layer or film of liquid on one side of a metallic surface, with heat supplied to the other side. Heat can be supplied by either steam or heated oil; heated oils are used to heat the waste to temperatures higher than can be achieved with saturated steam (>100°C).

The unique feature of this equipment is not the thin film itself (falling- and rising-film evaporators use thin liquid layers) but rather the mechanical agitator device for producing and agitating the film. This mechanical agitator permits the processing of high-viscosity liquids and liquids with suspended solids. The agitation at the heat transfer surface not only promotes heat transfer but also maintains precipitated or crystallized solids in manageable suspension without fouling the heat transfer surface.

There are two general types of mechanically agitated thin film evaporators: horizontal and vertical. A typical unit consists of a motor-driven rotor with longitudinal blades which rotate concentrically within a heated cylinder.

The vertical design illustrated in Figure 2 is manufactured by Luwa Corporation (Charlotte, NC) and incorporates a cylindrical thermal zone. Some manufacturers utilize a tapered thermal zone, as illustrated in Figures 3 and 4.

In the vertical design, Figure 5, product enters the feed nozzle above the heated zone and is mechanically transported by the rotor and gravity down a helical path on the inner heat transfer surface.

The evaporator does not operate full of product; the liquid or slurry forms a thin film or annular ring of product from the feed nozzle to the

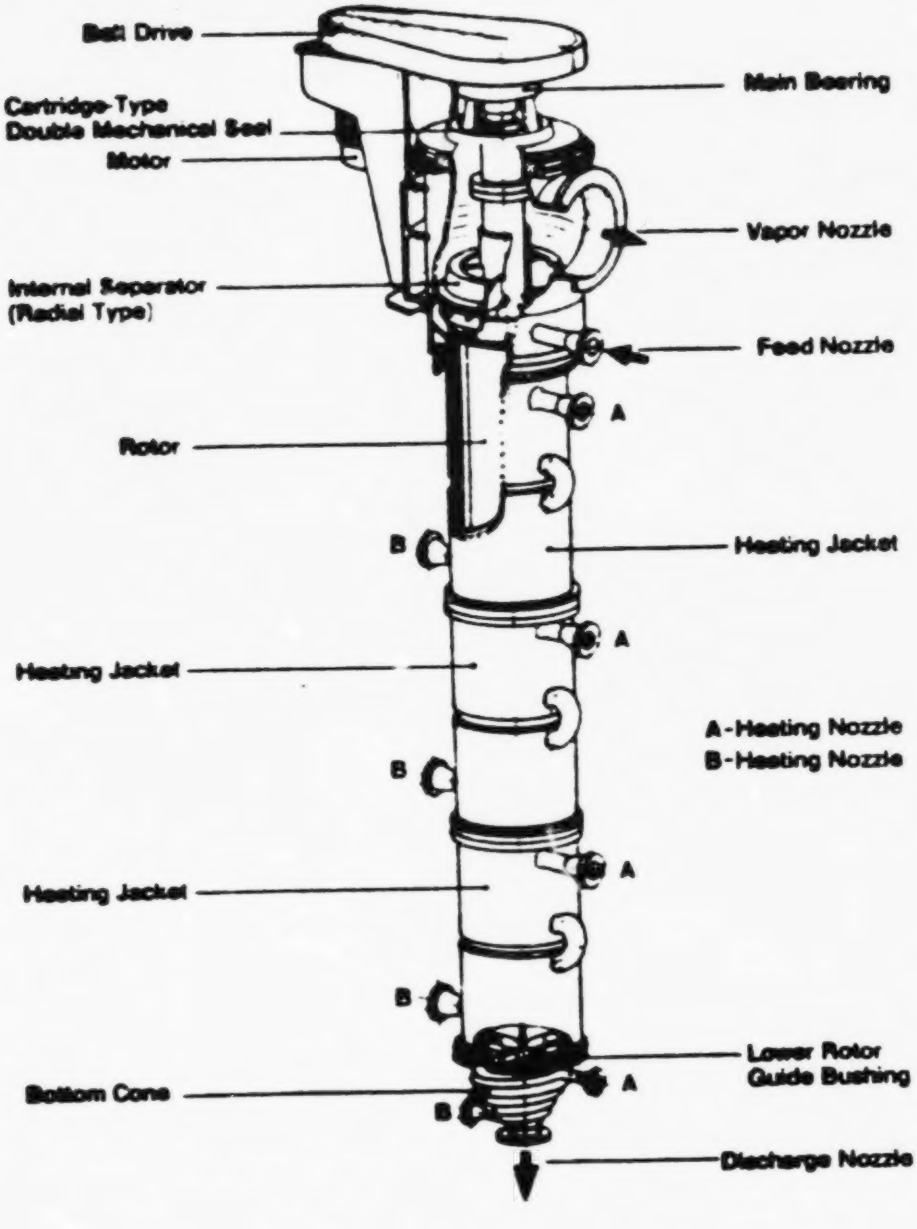

Belt Drive
Main Bearing
Cartridge-Type Double Mechanical Seal
Motor
Vapor Nozzle
Internal Separator (Radial Type)
Feed Nozzle
A
Rotor
Heating Jacket
B
A
Heating Jacket
A-Heating Nozzle
B-Heating Nozzle
B
A
Heating Jacket
B
Lower Rotor Guide Bushing
A
Bottom Cone
B
Discharge Nozzle

Figure 2. Vertical thin-film evaporator, cylindrical thermal zone.

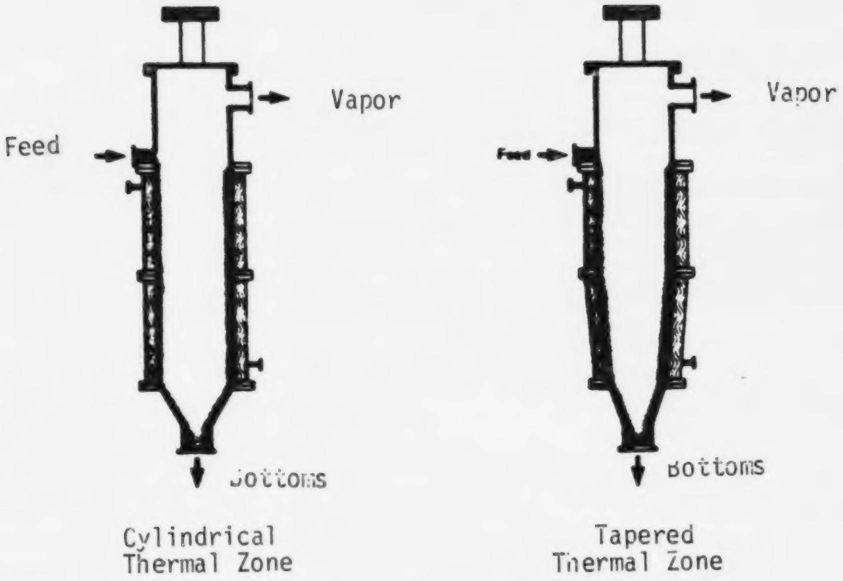

Vapor
Feed
Bottoms
Cylindrical Thermal Zone
Vapor
Feed
Bottoms
Tapered Thermal Zone

Figure 3. Vertical thin-film evaporators.

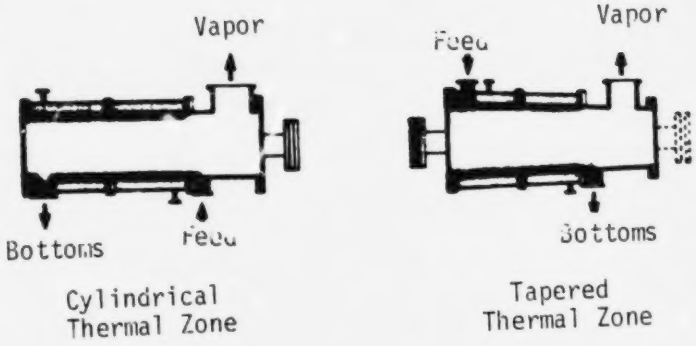

Vapor
Bottoms
Feed
Cylindrical Thermal Zone
Vapor
Feed
Bottoms
Tapered Thermal Zone

Figure 4. Horizontal thin-film evaporation.

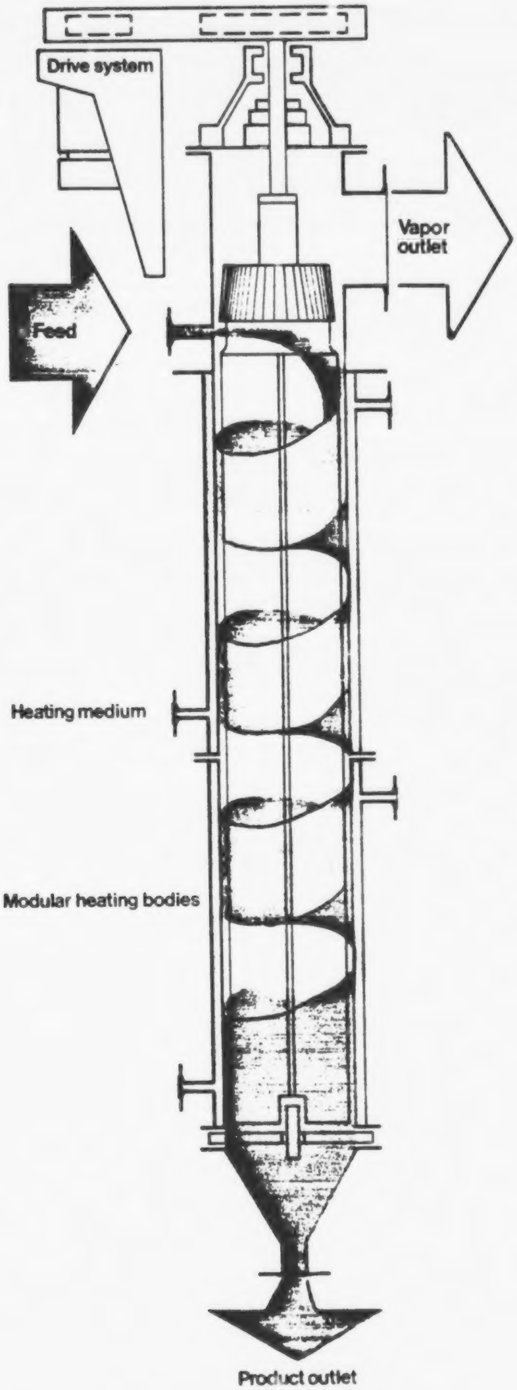

Drive system
Vapor outlet
Feed
Heating medium
Modular heating bodies
Product outlet

Figure 5. Flow path of thin-film evaporator.

product outlet nozzle, as illustrated in Figure 6. Holdup or inventory of product in a thin-film evaporator is very low--typically about a half-pound of material per square foot of heat transfer surface.

With typical tip speeds of 900 to 1,200 cm/sec (30 to 40 feet per second), centrifugal forces distribute the liquid feed as a thin film on the heated cylinder wall, and the wave action produced by the rotating blades provides rapid mixing and frequent surface regeneration of the thin liquid layer on the transfer surface.

As illustrated in Figure 7, the rotor may be one of several "zero-clearance" designs, a rigid "fixed-clearance" type, or, in the case of tapered rotors, an adjustable clearance construction may be used. The clearance is the space between the shell and the periphery of the circle described by the rotor blade tips. One vertical design includes an optional residence time control ring at the end of the thermal surface to hold back (and thus build up) the film thickness.

Mechanical construction of units with a fixed clearance rotor requires machining of both the shell inside diameter and the outside diameter of the rotor to assure concentricity and dynamic balancing of the rotor, and consideration of the effects of differential expansion of rotor and shell. Although clearances may vary in a narrow range determined by viscosity, surface tension, and thermal conductivity of the material handled, they usually fall in the range of 0.08 to 0.25 cm (0.03 to 0.10 inches). Such small clearances emphasize the importance of the machining operations.

Adjustable clearance is available in the tapered shell units by moving the rotor in or out with respect to the fixed position of the shell (see Figure 8). This offers some advantage in a pilot plant or commercial unit where a wide variety of materials will be processed.

"Zero-clearance" or wiping blades are spring-loaded or free-floating and are forced against the wall by centrifugal force as the agitator rotates. This design is primarily for materials that remain in a liquid state at the final concentration. Kontro, however, has designs suitable for materials that will be evaporated to the solid state.

PERFORMANCE

Heat-transfer rates between the liquid and the wall (termed its "U-value"), in most situations, determine the size and effectiveness of thin-film equipment. Figure 9 shows overall U-values of several dozen products, differing in latent heat of vaporization, heat conductivity, viscosity, boiling-point rise, and surface tension. These data were developed using saturated steam or high-temperature heating mediums. The U-values include the resistance of a 0.63 cm (1/4 in.) stainless steel wall or a 1.3 cm (1/2 in.) stainless steel clad wall. A U-value can be used to calculate the temperature of the heating fluid necessary to achieve a specified flow of overhead product.

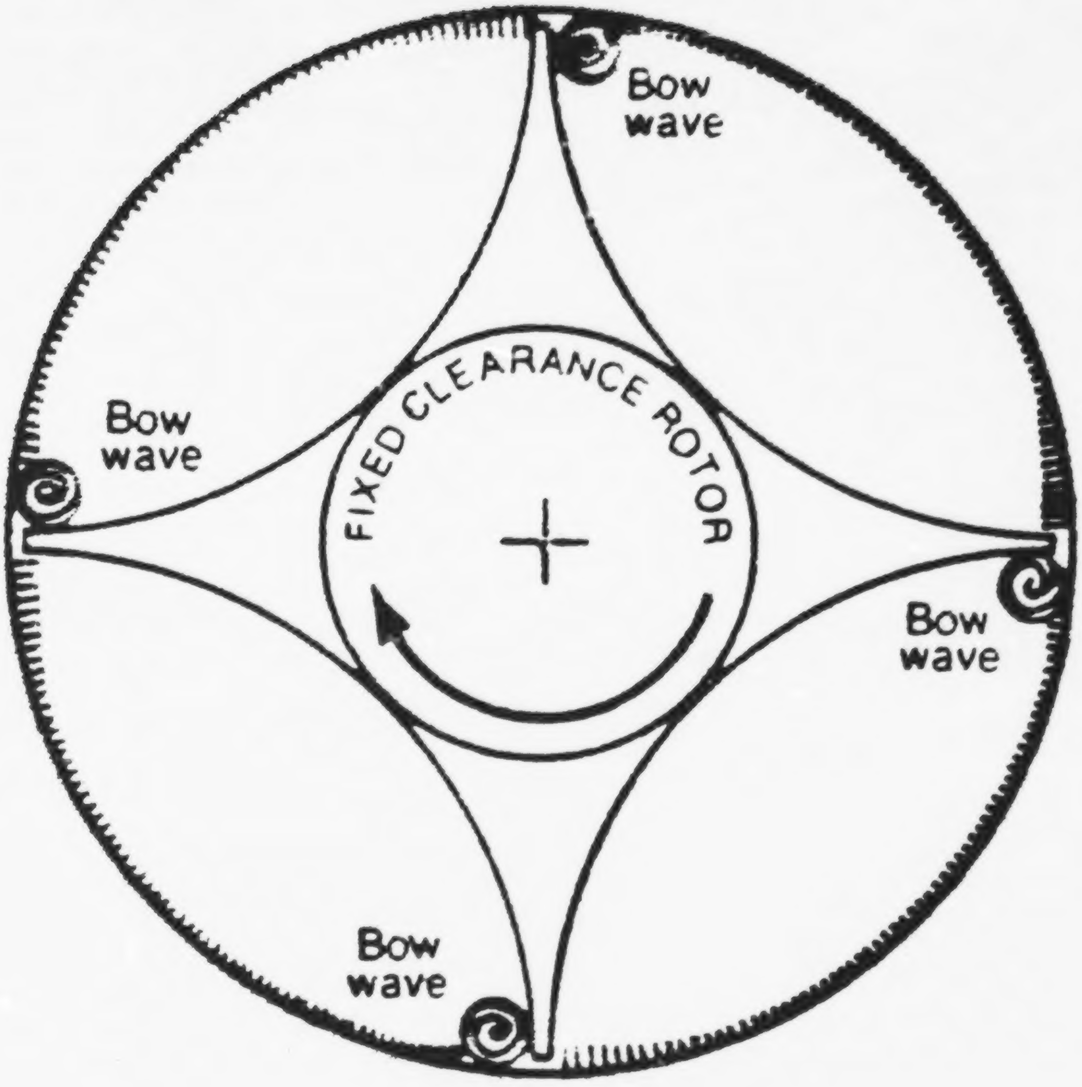
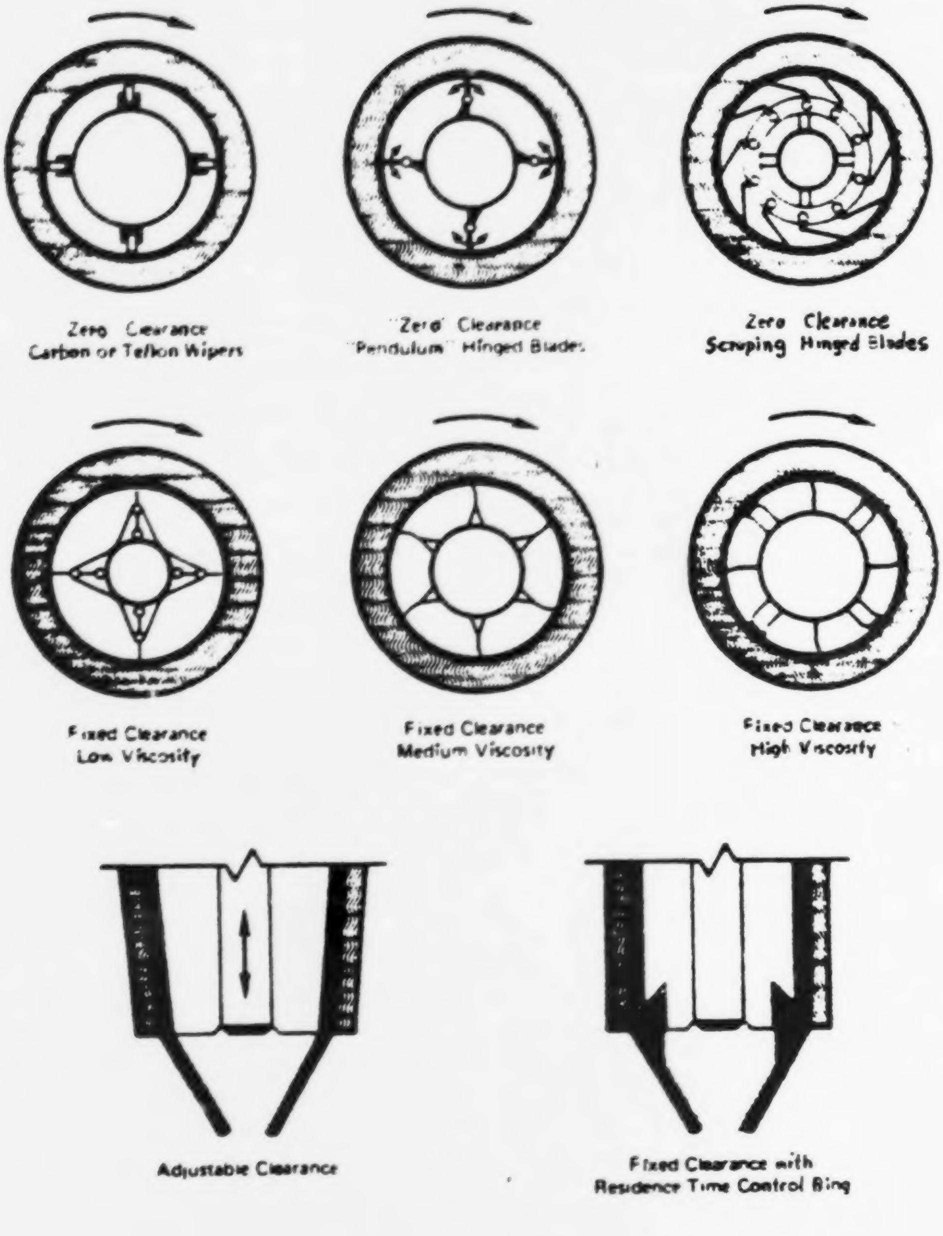

Bow wave
Bow wave
FIXED CLEARANCE ROTOR
Bow wave
Bow wave

Figure 6. Cross section of thin-film evaporators.



Zero Clearance
Carbon or Teflon Wipers

"Zero" Clearance
"Pendulum" Hinged Blades

Zero Clearance
Scraping Hinged Blades

Fixed Clearance
Low Viscosity

Fixed Clearance
Medium Viscosity

Fixed Clearance
High Viscosity

Adjustable Clearance

Fixed Clearance with
Residence Time Control Ring

Figure 7. Rotors for thin-film evaporators.

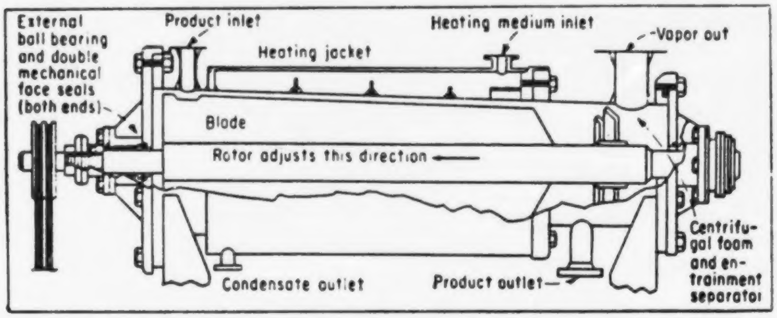

External ball bearing and double mechanical face seals (both ends)
Product inlet
Heating medium inlet
Vapor out
Heating jacket
Blade
Rotor adjusts this direction
Centrifugal foam and entrainment separator
Condensate outlet
Product outlet

Figure 8. Kontro horizontal design has adjustment for rotor-shell clearance.

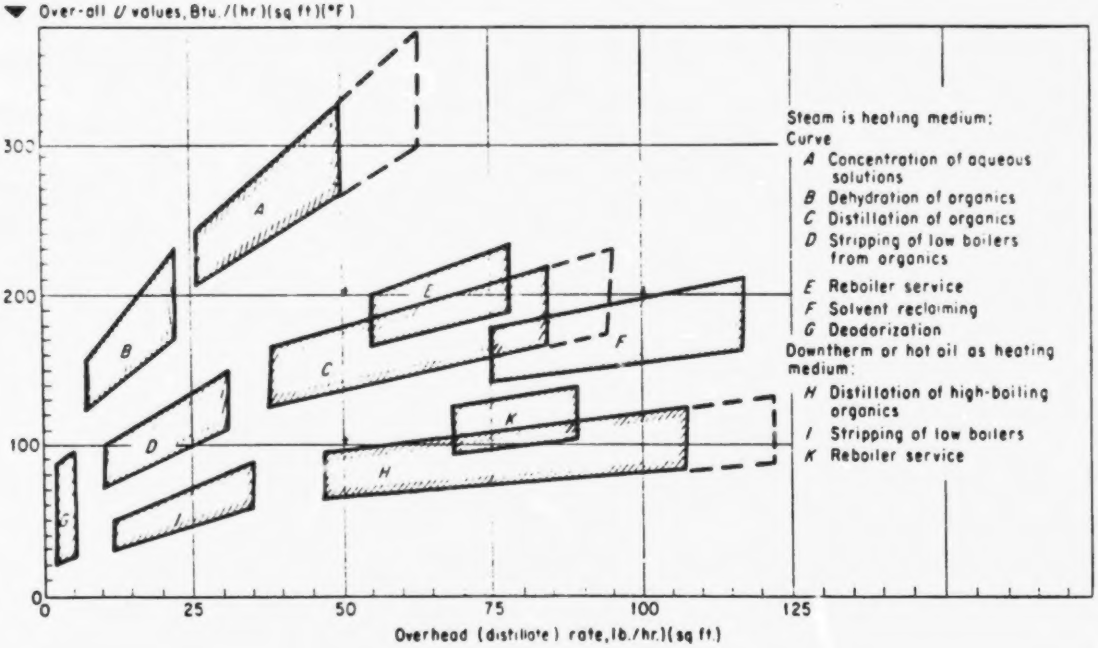


Figure 9. Heat transfer in agitated thin-film equipment for various services. (Fischer, 1965)

The heat-transfer coefficients are grouped into main applications to facilitate preliminary evaluations. U-values for concentration or distillation show the characteristic increase with increased heat flux, due to the additional circulation of the formed vapor bubbles (nucleate boiling usually takes place in thin-film evaporators).

A direct comparison of the Figure 9 U-values with coefficients for conventional equipment would not be too meaningful, since products handled in falling-film evaporators usually have low viscosities while the values in Figure 9 are for viscosities ranging up to 10,000 cp under operating shear (equivalent to 100,000 to 400,000 cp without subjected shear, as measured by standard instruments in the laboratory).

In many applications of the agitated thin-film evaporator, mass transfer (not heat transfer) determines the size and capacity of the equipment. Deodorization, low-boiler stripping, and dehydration are mass transfer controlled processes. The stripping of volatile organics from hazardous waste falls within this category, if it is desired to remove the volatiles to low residual levels.

A volatile component has to be transported within the film to the interface, then vaporized. Transport of the volatile component within the film is accomplished by molecular diffusion or by eddy diffusion. Molecular diffusion, the only possibility in nonagitated laminar flow, is extremely slow and decreases linearly with increasing viscosity of the film liquid. Eddy diffusion can be influenced and increased by adding turbulence to the film. Values of diffusivities in agitated thin-film evaporators are on the order of 10^{-6} m^2/sec, or 1,000 to 10,000 times greater than the molecular diffusivities achieved in nonagitated evaporators.

Deodorization is an extreme stripping operation where only traces of a low-boiling odor impurity in a feedstock must be removed. Again, it is the diffusion process, not the thermal load, that determines the required surface. Deodorization can be further facilitated by using a stripping gas (or steam) to lower the partial pressure of the low-boiling impurities.

Typical operating characteristics for various applications of thin-film evaporators are listed in Table 10.

SUPPLIERS

There are six major producers of agitated thin-film equipment in the United States: Buflovak Division of Blaw-Knox, Chemetron Division of Cherry Burrell, Luwa, Kontro, Pfaudler, and Artisan. The locations of these companies are presented in Table 11. The Luwa concern had the first production units onstream in 1946 in Switzerland. The Pfaudler design is based on development work by Arthur Smith. Buflovak introduced its design with a bottom drive in the mid-fifties. The tapered shell designs of Kontro (Figure 8) evolved from the standard cylindrical designs. Basic design configurations furnished by the six producers are shown in Table 12. This table also relates liquid-vapor flow characteristics to design and location of the vapor separator. Countercurrent flow occurs when the vapor is removed

TABLE 10. TYPICAL OPERATING CHARACTERISTICS FOR THIN-FILM UNITS

SIZE: 1 to 430 square feet of heat transfer surface.

CAPACITY: Steam heated:
- Water evaporation, 60 kW/m^2 (50,000 Btu/(hr) (sq ft))
- Organics distillation, 63 kW/m^2 (20,000 Btu/(hr) (sq ft))

Hot oil heated: organics distillation, 25 kW/m^2 (8,000 Btu/(hr) (sq ft))

OPERATING PRESSURE: Standard (full vacuum to atmospheric pressure)
Special (any positive pressure)

HEATING STEAM IN JACKETS: Up to 1.4 MPa (200 psig)

MAXIMUM HOT-OIL TEMPERATURE: Up to 350°C (650°F)

LIQUID THROUGHPUT: Up to 900-1,100 kg/m^2 (200-250 lb/(hr) (sq ft))

PRESSURE DROP (VAPOR FLOW): 0.5 mm Hg

OVERHEAD TO BOTTOMS SPLITS: Up to 100 to 1

RESIDENCE TIME: Uncontrolled, 3 to 10 sec. Controlled, 3 to 100 sec.

PRODUCT VISCOSITIES: Up to 10,000 cp. at operating conditions

BLADE TIP SPEED: Nonscraping blades, 9 to 12 m/sec (30 to 40 ft/sec)
Scraping blades, 1.5 to 3 m/sec (5 to 10 ft/sec)

RECOMMENDED MAINTENANCE: Twice a year, more often when processing extreme products.

TABLE 11. MAJOR AGITATED THIN FILM EVAPORATOR PRODUCERS

Blaw-Knox (Buflovak Division)	Buffalo, NY
Cherry Burrell (Chemetron Division)	Louisville, KY
Luwa	Charlotte, NC
Kontro	Orange, MA
Pflaudler	Rochester, NY
Artisan Industries, Inc.	Waltham, MA

TABLE 12. CONFIGURATIONS OF COMMERCIAL AGITATED THIN FILM UNITS

Configuration	Manufacturer	Liquid-vapor flow
Vertical, cylindrical shell integral separator	Luwa Chemetron	Countercurrent Countercurrent
Vertical, cylindrical shell external separator	Buflovak	Cocurrent
Vertical, cylindrical shell, internal separator and condenser	Pfaudler	Separated
Horizontal, tapered shell, integral separator	Kontro	Co- or Countercurrent
Vertical, tapered shell, integral separator	Kontro	Co- or Countercurrent
Horizontal, cylindrical shell, external separator	Artisan	Co- or Countercurrent

from the top of the evaporator and the bottoms are removed from the bottom; both the liquid and vapors flow in the same direction in co-current flow. In separated flow, the vapors are condensed in an internal condenser.

LUWA CORPORATION

Luwa is a major producer of thin-film evaporators in the United States. Plants A and C (Section 8) used Luwa stills to process waste. The following section discusses Luwa stills, but the general principles may apply to other producers.

Design

Luwa manufactures vertical thin-film evaporators with cylindrical heating bodies (see Figure 2). The body of each Luwa thin-film evaporator is made in sections, including one or more jacketed thermal sections, a top or vapor head, and a bottom discharge cone. The thermal body sections must have a uniform bore for precise rotor clearance. The sections are rolled, machined, and honed (or bored), and then are assembled as a unit.

The general design specifications for standard Luwa evaporators are:

Pressure:	Full vacuum to about 15 psig
Temperature:	To 340 degrees C (650 degrees F)
Heating:	Steam to 1.4 megapascal (200 psig) Dowtherm to 1.0 megapascal (150 psig)
Sizes:	0.13 to 40 M^2 (1.4 to 430 ft^2) of surface

Figure 10 lists the specific design data for all standard Luwa evaporators.

At the drive end of the rotor, a double mechanical seal is most often supplied, although single mechanical seals can be used satisfactorily. A coaxial design like the Crane 151 seal, which is more durable and accommodates more vibration, has a typical life expectancy of about 4 years. Because of torque and some axial loading by the multiple belt drive, a self-aligning roller bearing is recommended; it also has a life of about 4 years. The bearing and seal can be inspected and serviced without removing the top cover or rotor.

Reasons for premature failure are:

Double Mechanical Seal

- loss of cooling fluid
- solids or abrasives in the seal coolant
- chemical attack on elastomeric O-ring
- abnormal vibration

	APPROXIMATE DIMENSIONS IN INCHES (MILLIMETERS)					HEAT TRANSFER SURFACE SQ FT (m²)
EVAPORATOR MODEL	A	B	C	D	E	
LN-0012	44 (1117)	3 (82)	30 (762)	34 (863)	10 (255)	1 4 (0 13)
LN-0050	72 (1830)	7 (180)	38 (965)	81 (2057)	20 (500)	5 4 (0 50)
LN-0100	95 (2413)	10 (250)	54 (1372)	114 (2896)	23 (585)	10 8 (1 0)
LN-0200	128 (3250)	14 (360)	84 (2133)	135 (3429)	27 (685)	21 6 (2 0)
LN-0350	180 (4572)	17 (430)	125 (3175)	193 (4902)	48 (1210)	37 7 (3 5)
LN-0500	204 (5181)	20 (500)	144 (3657)	217 (5512)	49 (1250)	53 8 (5 0)
LN-0750	248 (6300)	24 (600)	180 (4580)	270 (6850)	59 (1500)	80 7 (7.5)
LN-1050	294 (7467)	28 (710)	220 (5588)	295 (7500)	67 (1700)	113 0 (10 5)
LN-1400	320 (8128)	34 (850)	250 (6350)	341 (8661)	87 (2200)	150 7 (14 0)
LN-1800	347 (8814)	39 (1000)	271 (6884)	366 (9300)	99 (2500)	193 7 (18 0)
LN-2400	381 (9680)	47 (1200)	301 (7650)	404 (10260)	119 (3000)	258 2 (24 0)
LN-3200	435 (11050)	55 (1400)	344 (8737)	457 (11600)	138 (3500)	344 3 (32 0)
LN-4000	472 (11989)	67 (1700)	373 (9475)	492 (12500)	168 (4250)	430 4 (40 0)

	APPROXIMATE WEIGHT LBS (KG)			JACKET PRESSURE RATING PSIG		ROTOR DRIVE MOTOR STANDARD H P
EVAPORATOR MODEL	COMPLETE ASSEMBLY		TOP COVER WITH ROTOR	AT SATURATED STEAM	AT 650 F	
	EMPTY	FLOODED				
LN-0012	143 (65)	150 (68)	55 (25)	200	150	1 5
LN-0050	770 (350)	850 (385)	155 (70)	200	150	3 0
LN-0100	1015 (460)	1170 (530)	275 (125)	150	100	5 0
LN-0200	1740 (790)	2270 (1030)	480 (218)	150	100	7 5
LN-0350	3525 (1600)	4400 (2000)	1060 (480)	150	100	7 5
LN-0500	4520 (2050)	6050 (2750)	1150 (520)	150	100	10
LN-0750	6950 (3150)	9700 (4400)	1670 (850)	150	100	15
LN-1050	13200 (6000)	19000 (8600)	2425 (1100)	150	100	20
LN-1400	17200 (7800)	25000 (11350)	4125 (1870)	150	100	20
LN-1800	23100 (10500)	35600 (16150)	5800 (2630)	150	100	25
LN-2400	33100 (15000)	51150 (23200)	8400 (3800)	150	100	30
LN-3200	48500 (22000)	79600 (36100)	11000 (5000)	125	100	40
LN-4000	63900 (29000)	111400 (50500)	15650 (7100)	125	100	50

A. Overall unit height
B. Inside diameter
C. Support elevation to bottom nozzle
D. Clearance from support elevation for removing rotor
E. Maximum width

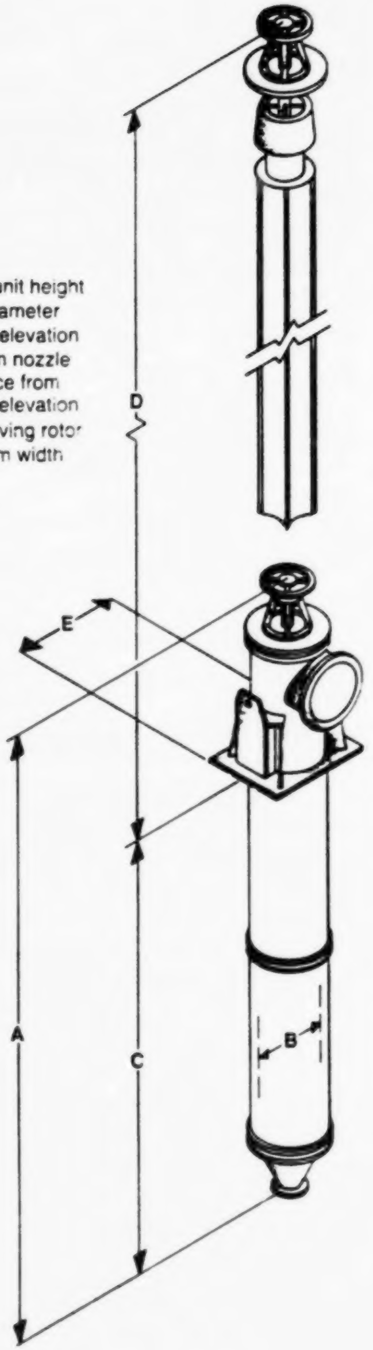


Figure 10. LUWA evaporator design data.

Self-Aligning Roller Bearing

- inadequate lubrication
- mixing of lubricant types
- sporadic lubrication which could permit water or other fluids into bearing
- abnormal vibration

The internal bearing most commonly used at the discharge end is a nonload bearing design. The full weight of the rotor is supported at the top, and the spider-type bearing assembly only centers the rotor. A hardened pin on the rotor fits into a carbon cup bushing in the center of the spider. This bearing design is preferred to an external bearing to eliminate a mechanical seal and bearing at the dirty end of the machine. This design often employs a small amount of lubricant: oil, process liquid, water, steam, or air. Typical life of the carbon bushing is 2 years. The bearing can be inspected or serviced by simply removing the bottom cone.

Premature failure of the bearing can be caused by the following:

loss of lubricant,

poor lubricating properties of lubricant, or

process upsets with liquid backing up into rotor area.

Original equipment rotors last typically 10 to 30 years with little or no maintenance.

Capital Costs

Listed in Table 13 are 1984 budget prices for four standard Luwa evaporators with 316 L stainless steel wetted parts.

Table 14 compares the cost of the evaporator alone to the system installed cost for two cases. In the case designated "simple," the heating medium is assumed to be steam and the system is controlled manually. In the case designated "sophisticated," the heating medium is a recirculating thermal fluid and the system is completely automated. The cost of a heat generator (steam boiler) is not included.

Table 14 gives a very generalized example based, however, on actual projects involving agitated thin-film evaporators. From Table 14 we can say that installed cost could range from twice the evaporator-only cost to as high as four times, depending upon the degree of sophistication.

Operating Costs

As an example of operating costs, assume that a hazardous waste containing 2 percent by weight volatile organics, 88 percent by weight water, and 10 percent by weight solids is to be processed in a steam-heated thin-film evaporator to remove the volatile organics. Assume that the limiting factor

TABLE 13. BUDGET PRICES[a]--LUWA EVAPORATORS

Model number	Heating surface m^2 (sq ft)	Budget price (1984)
LN-0012	0.13 (1.4)	$ 16,000
LN-0100	1.0 (10.8)	45,000
LN-0500	5 (53.8)	120,000
LN-1400	14 (150.7)	210,000

[a] Budget prices are for used equipment.

TABLE 14. COST DISTRIBUTION OF AGITATED THIN FILM UNITS[a]

	Simple[b]	Sophisticated[b]
Evaporator	100	100
Components as % of evaporator		
Main auxiliaries (condenser, pumps, vacuum system, controls)	30	150
Piping, fittings (materials only)	10	20
Structural frame	5	5
Installation (foundation, erection, piping, wiring, insulation)	100	100
TOTAL INSTALLED COST	245	375
Evaporator as % of installed cost	41	27

[a] ATI, 1984; does not include steam boiler.

[b] Sophisticated has automatic controls; simple is manually operated.

in the degree of separation is a solids content of 50 percent by weight, above which the concentrates will not flow from the evaporator.

In this situation the residual level of organics in the concentrates will depend upon the vapor pressure of the organics, the viscosity of the concentrates, the speed of the evaporator rotor, the heating temperature, and the operating pressure, but residual levels of 1,000 ppm and less could be expected for low-boiling organics. Assume a continuous feed flow rate of 40 liters (10 gallons) per minute is to be processed. Table 15 lists estimated operating costs and assumptions.

SOURCES OF EMISSIONS TO THE ENVIRONMENT

A thin-film evaporator system has three streams which exit the system--the distillate which was evaporated and then condensed back to the liquid phase, the concentrates stream which was not evaporated, and the noncondensible gases which are vented from the condenser.

In the case of volatile organics removal from hazardous waste, the distillate will contain the organics which have been removed from the waste. Depending upon water content and miscibility, it may be possible to separate the organics and water by decanting. The organics can be incinerated or reused, depending upon purity. In cases where fractionation of the organics into individual components is desired, vapors from the thin-film evaporator can be used as feed for a fractionation column. In some cases, it may be desirable to pass the distillate of the thin-film evaporator through activated carbon to remove the organics by adsorption. The bottoms product from the evaporator may be stripped of organics to levels which will allow it to be discharged to a municipal wastewater treatment system with the associated emissions of volatiles to the atmosphere.

The exhaust vent of the condenser contains noncondensible gases (primarily air) and potentially, a small amount of organic vapors which may pass through the condenser without condensing. This exhaust can be further processed by passing it through activated carbon to remove the organics by adsorption.

The exhaust vent of the condenser is connected to a vacuum pump when the evaporation is under vacuum. The vacuum pump vent is then a source of potential emissions. At startup, the vent emissions are expected to be greater than during normal operation.

APPLICATIONS TO PRETREATMENT

Thin-film evaporators can be used to remove volatile organic components from waste streams. The bottoms of the evaporator will have less volatiles than the feed, either because of the reduction in concentration or the reduction in the volume (or both). For mixed (water and organics) waste streams, a thin-film evaporator can selectively remove the water (the organics are high boiling) to improve the Btu value of the bottoms so that they can be more easily incinerated, or selectively remove the organics (the organics are low boiling) so that the organics can be recycled or burned.

TABLE 15. ESTIMATED OPERATING COSTS FOR VOLATILE REMOVAL FROM HAZARDOUS WASTE

Assumptions:	
Feed rate	40 L/min (10 gpm) continuous
Feed composition	10% solids, 2% organics, 88% water
Feed temperature	42°C (60°F)
Bottoms concentration	50% solids, less than 1,000 ppm organics
Steam pressure	1 M pascal (150 psig), saturated
Heat transfer coefficient	4 MJ/hr/m^2/°C (200 Btu/hr ft^2°F)
Luwa evaporator model	LN-1400
Steam cost	\$4.4/Mg (\$2/1,000 lb)
Electricity cost	\$0.05 kWh
Labor cost (includes overhead)	\$20/man-hour
Operators required	0.25 (automated system)
Operating period	8,760 hr/yr
Operating costs:[a]	
Steam	\$85,000/yr
Electricity	7,500/yr
Operating labor	45,000/yr
Spare parts	10,000/yr
Maintenance	10,000/yr
Total	\$157,500/yr
Unit costs:	
\$/L waste treated	0.0075
\$/L VOC removed	0.37
\$/Mg VOC removed[b]	462

[a] Does not include laboratory analyses and residual disposal costs.

[b] Assumes a density of 0.8 g/cm^3.

In the removal of volatiles from aqueous or mixed hazardous wastes, the removal efficiency of the volatiles and the residual volatile concentration will depend upon waste viscosity and concentration, the boiling points of the volatiles, and evaporator operating pressure and temperature. However, residual volatile concentrations of less than 1,000 ppm have been achieved routinely in similar applications, and less than 100 ppm is possible if conditions are optimal.

For complete separation of close-boiling components by distillation, a fractionation column of adequate design can be added to an agitated thin-film evaporator, which serves as a reboiler. A thin-film evaporator with vapors flowing countercurrent to the thin liquid film can be expected to have a fractionation effect of 1.25 to 1.5 theoretical plates, as opposed to the single plate maximum efficiency of a conventional still-pot reboiler.

SECTION 6

FRACTIONATION DISTILLATION AS A METHOD FOR PRETREATMENT OF HAZARDOUS WASTE STREAMS

INTRODUCTION

Distillation is an operation which has been in wide use throughout the chemical and petroleum industries for many years. In numerous cases, distillation is the only feasible method for separation of components in liquid or gas streams. Distillation systems vary in complexity from simple batch processes to very sophisticated multiple column units, with the system configuration depending upon the objectives of the operation.

By far, the most numerous industrial applications of distillation have been for purification in chemical manufacturing and in processes involving internal solvent recycle. The increasing difficulty and cost for disposal of chemical wastes, combined with the rising cost of raw materials during recent years, has made distillation more attractive as a process for recovery of organic solvents from waste streams which otherwise would be discarded.

PROCESS DESCRIPTION

Distillation is broadly defined as the separation of more volatile materials from less volatile materials by a process of vaporization and condensation. In engineering terminology, the separation of a liquid from a solid by vaporization is considered evaporation, and the term "distillation" is reserved for the separation of two or more liquids by vaporization and condensation.

Basic distillation involves application of heat to a liquid mixture, vaporization of part of the mixture, and removal of heat from the vaporized portion. The resultant condensed liquid, the distillate, is richer in the more volatile components, and the residual unvaporized bottoms are richer in the less volatile components. Most commercial distillations involve some form of multiple staging in order to obtain a greater enrichment than is possible by a single vaporization and condensation operation.

Simple distillations use a single equilibrium stage to obtain separation and may be either batch or continuous. Simple continuous distillation (also called flash distillation) has a continuous feed to an equilibrium stage; the liquid and vapor leaving the stage are in equilibrium. Flash distillation is used in applications where a crude separation is adequate. The component separation in simple distillation is limited by thermodynamic partitioning constraints, and multiple staging must therefore be used to increase the component separation.

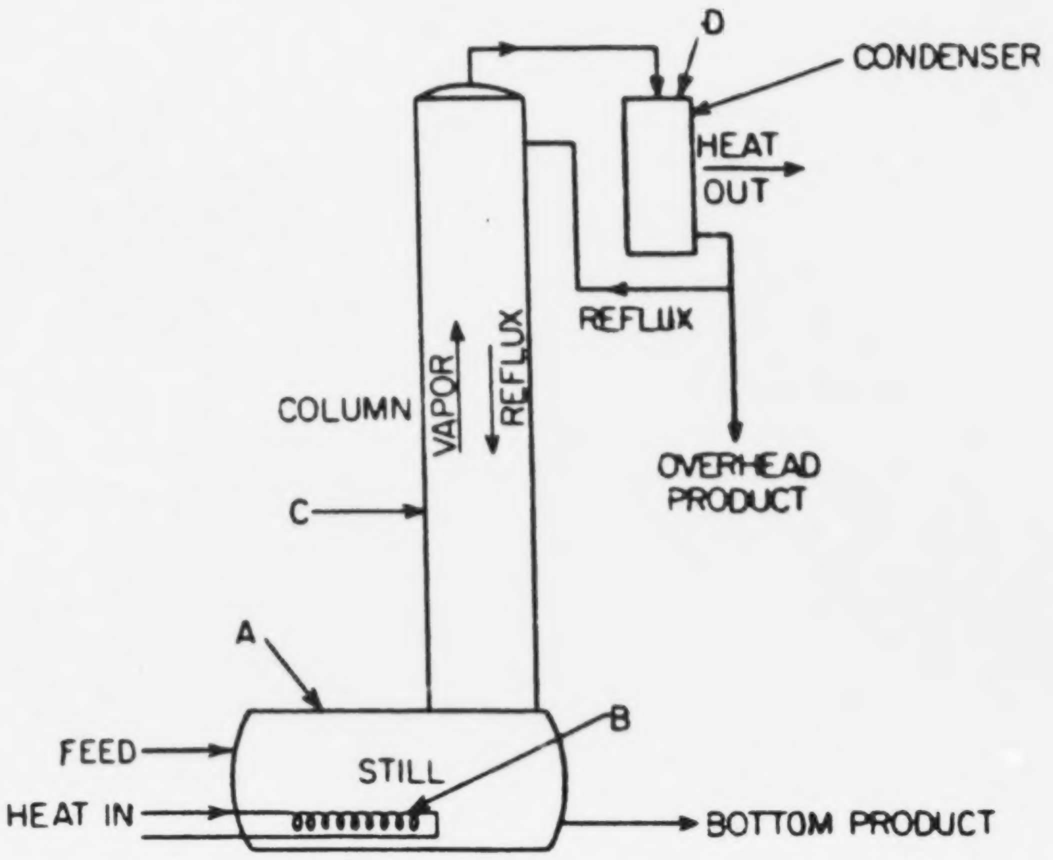
Multiple staging is achieved by returning part of the condensate to the top of the column under such conditions that this reflux is brought into intimate contact with the vapors on their way to the condenser. Either a tray or a packed column is normally used to provide adequate gas-liquid interfacial area for mass transfer. The degree of component separation for a given system configuration is dependent upon the operating conditions, the number of stages, and the amount of reflux. In continuous distillation, feed is constantly charged to the column at a point between the top and bottom trays. The section of the column above the feed point is called the rectifying or enrichment section and serves primarily to remove the heavier component from the upflowing vapor; it enriches the light overhead product. The portion of the column below the feed point is called the stripping section and serves primarily to remove or strip the light component from the downflowing liquid. The stripping section thus serves mainly to purify the bottoms product. In batch distillation, where fractionation is primarily for enrichment of the overhead product, only rectification is involved since there is no stripping section. Consequently, it is possible to obtain a distillate of high purity, but the recovery of the less volatile components from the bottoms is poor during the removal of the pure component. As the concentration of the more volatile component diminishes in the overhead vapor, the reflux ratio must increase to maintain a constant distillate composition. A point will be reached at which time the overhead vapor contains proportionally more of the less volatile components and it becomes necessary to divert the distillate to an intermediate product vessel so that the desired bottoms concentration can be achieved by further distillation without contaminating the low-boiling product which was initially distilled.

Batch Distillation

A typical batch distillation operation (see Figure 11) involves charging the feed batch initially to a still. The still is heated usually by steam coils, utilizing total reflux until the boiling point of the feed is reached and the column temperatures have stabilized (column head temperatures are the boiling point of the more volatile component or azeotrope). Takeoff of overhead product is then started. As the distillation proceeds, the more volatile component is continuously depleted from the still, building up in the distillate receiver. The temperature of the feed batch will rise during the distillation, approaching the boiling point of the less volatile components near completion. As the distillation proceeds and the concentration of the more volatile component increases in the overhead vapor, the reflux ratio must be increased in order to maintain a constant distillate composition. An alternative may be to maintain a constant reflux if distillate purity requirements of the more volatile component in the bottoms are required; it will be necessary to switch to an intermediate product tank and continue distillation after reflux can no longer maintain an acceptable distillate composition.

Continuous Distillation

A typical continuous distillation system (see Figure 12) consists of a reboiler, tray or packed column, condenser, accumulator, and associated pumps, piping, and instrumentation. The feed stream enters the column at a point


D
CONDENSER
HEAT
OUT
REFLUX
COLUMN
VAPOR
REFLUX
OVERHEAD
PRODUCT
C
A
B
FEED
STILL
HEAT IN
BOTTOM PRODUCT

Still with fractionating column: *A*, still; *B*, heating coil; *C*, column; *D*, condenser.

Figure 11. Batch distillation.

between the top and bottom plates. The plate on which the feed enters is called the feed plate. The section of the column above the feed plate is the rectifying section while the section below the feed plate is the stripping section. As the liquid moves down the stripping section, it encounters vapor moving up the column from the reboiler. The more volatile component is stripped from the feed, which continues downward to the column bottom and reboiler. The vapor rising through the rectifying section encounters liquid moving down this section as a result of reflux introduced at the top of the column. This enriches the more volatile component in the overhead vapor which flows from the top of the column through a condenser to an accumulator. Reflux is pumped from the accumulator back into the top of the column, with the remainder of the liquid distillate being taken off as overhead product. The reboiler in a typical continuous distillation process is normally heated with steam, and the stripped, more volatile component is continuously discharged from the vessel (see Figure 12).

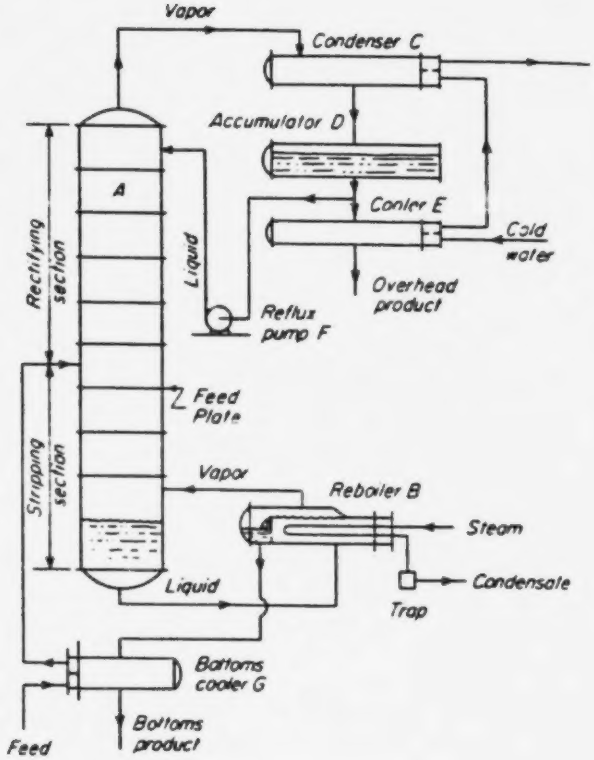
PROCESS DESIGN CONSIDERATIONS

In order to design or specify an optimum distillation system for a specified application, the feed stream characteristics and the overhead product and bottoms product purities must be defined. The feed rate, feed temperature, feed composition, component relative volatilities, and product purity determine, to a large extent, the size and cost of the system. The process design and operating conditions that will provide the optimum combination of capital and operational costs can be determined.

At offsite TSDFs, a variety of different waste streams will be treated. Several different columns can be employed at a TSDF, the selection of process columns depending on waste volume and difficulty of separation.

The number of plates or stages required for a given separation is dependent on the reflux rate. As the reflux is increased, the required number of stages falls. An infinite reflux ratio would be required at the minimum number of stages, and an infinite number of stages would be required at the minimum reflux required to effect the separation. The optimum process will obviously lie somewhere in between these extremes. As the reflux rate is increased, the required number of stages decreases, resulting in a lower cost for the column, even though the column diameter must increase to maintain an acceptable pressure drop with the increased vapor flow. However, as the reflux increases, reboiler steam requirements increase proportionately. Steam is the single biggest operating cost, accounting for over 50 percent of the variable cost. In addition, a larger reboiler and condenser are required, increasing the cost of these components. It has been found that the optimum reflux ratio generally will be between 1.1 and 1.25 times the minimum theoretical ratio (King, 1977).

At a TSDF, there is considerable flexibility in the selection of processing conditions. The reflux ratio, feed rate, and other variables can be specified to achieve a desired product composition. The feed rate has a direct effect on the reboiler capacity and the column diameter. The column diameter must be sized so that the pressure drop across the column will fall within the optimum operating range. The relative volatility of the feed


Vapor
Condenser C
Accumulator D
A
Liquid
Cooler E
Cold water
Rectifying section
Overhead product
Reflux pump F
Feed Plate
Stripping section
Vapor
Reboiler B
Steam
Condensate
Trap
Liquid
Bottoms cooler G
Bottoms product
Feed

Continuous fractionating column with rectifying and stripping sections.

Figure 12. Continuous distillation.

stream components will directly affect the number of stages required at a set reflux rate. The feed stream temperature and component physical property considerations will influence the location of the feed point in the column.

EQUIPMENT DESIGN

After a distillation process has been designed to achieve a specific separation for a particular feed stream, there are a number of different equipment types available for the system components. Consideration may be given to such factors as fouling tendency, corrosivity, throughput, versatility, and cost in selecting the best equipment designs for the process. The following discussion briefly outlines the many pieces of hardware required for a distillation system and the many equipment variations available to meet different process conditions. (This section is based on information contained in the APV Distillation Handbook.)

Column Shells

A distillation column shell can be designed either as a free-standing module or to be supported by a steel structure. A self-supporting column is generally more economical. Column fabrication in a single piece (without shell flanges) is more economical than with shell flanges, in addition to simplifying installation and eliminating potential sources of leakage. Columns over 80 feet (24 m) in length have been shipped by road without transit problems. Hazardous waste processing may require a flange assembly to facilitate cleaning.

While columns of over 3 feet (1 m) in diameter normally have been transported without trays to prevent dislodgement and possible damage, recent and more economical techniques have been devised for factory installation of trays with the tray manways omitted. Manways are added after the column has been erected, and the fitter inspects each tray. The position and number of manways are important, especially for systems which require periodic cleaning.

Packing can be installed prior to shipment in columns of 20-in. (51 cm) in diameter or less which use high-efficiency metal mesh packing. Larger columns are packed on site to prevent the packing from compacting during transit and leaving voids. Random packing is almost always installed on site.

Additional requirements can include access platforms and interconnecting ladders for onsite attachment to free-standing columns.

Column Internals

During recent years, the development of sophisticated computer programs and new materials has led to many innovations in the design of trays and packings for more efficient operation of distillation columns.

Tray Devices--

There are five basic types of distillation trays: sieve, valve, bubble cap, dual flow, and baffle trays--each with unique advantages and preferred usages. Sieve and valve type trays currently are most often specified for tray towers.

The hydraulic design of a tray is a most important factor. The upper operating limit generally is governed by the flood point although, in some cases, entrainment also can restrict performance. Entrainment reduces concentration gradients because some liquid flows up the column, therefore lowering efficiency. A column also can flood by downcomer backup. The trays fill and the pressures increase when the downcomer is unable to handle all the liquid involved. This can occur with a highly foaming liquid. Flooding is associated with high tray pressure drops and small tray spacings.

The lower limit of tray operations is characterized by the excessive liquid weeping from one tray to the next. Unlike the upward transport of liquid via entrainment, weeping liquid flows in the normal direction, and considerable amounts can be tolerated before column efficiency is significantly affected. As the vapor rate decreases, however, a point eventually is reached when all the liquid is weeping, and there is no liquid seal on the tray. This is known as the dump point, below which there is a severe drop in efficiency.

Sieve Tray--The sieve tray (see Figure 13) is a low-cost device which consists of a perforated plate that usually has holes of 0.5 to 2.5 cm (3/16 to 1 in.) in diameter, a downcomer, and an outlet weir. Although inexpensive, a correctly designed sieve tray can be comparable to other tray styles in vapor and liquid capacities, pressure drop, and efficiency. Its flexibility, however, is inferior to valve and bubble cap trays, and it is sometimes unacceptable for low liquid loadings when weeping has to be minimized.

Depending upon process conditions and allowable pressure drop, the turndown ratio of a sieve tray can vary from 1.5 to 3 and may be occasionally higher. Ratios of 5 or greater can be achieved only when the tray spacing is large, the available pressure drop is very high, the liquid loadings are high, and the system is nonfoaming. For many applications, a turndown ratio of 1.5 is quite acceptable.

It also is possible to increase the flexibility of a sieve tray column for occasional low throughput operation by maintaining a high reboil and increasing the reflux ratio. This may be economically advantageous when the low throughput occurs for a small fraction of the operating time. Flexibility likewise can be increased by the use of blanking plates to reduce the tray hole area. This is particularly desirable for initial operation of a column in situations where it is envisioned that the plant capacity will be expanded after a few years. There is no evidence to suggest that blanked-off plates have inferior performance to unblanked plates of similar hole area.

Dual Flow Tray--The dual flow tray is a high-hole-area sieve tray without a downcomer. The downflowing liquid passes through the same holes as the rising vapor. Since no downcomer is used, the cost of the tray is lower than that of a conventional sieve tray.

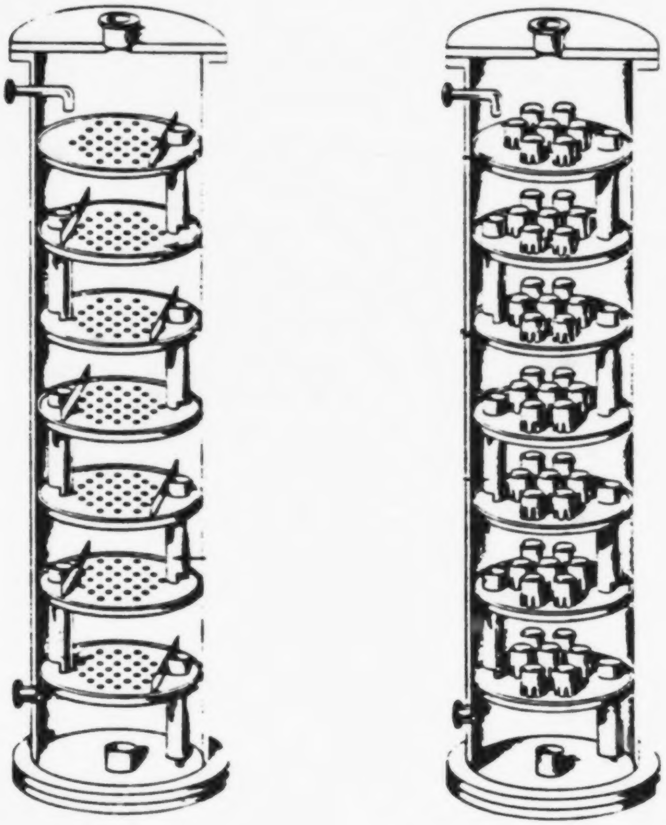


Figure 13. Sieve tray column (left). Bubble tray column (right).

In recent years, use of the dual flow tray has declined somewhat because of difficulties experienced with partial liquid/vapor bypassing of the two phases, particularly in large diameter columns. The dual flow column also has a very restricted operating range and a reduced efficiency because there is no cross-flow of liquid.

Valve Tray--While the valve tray dates back to the rivet type first used in 1922, many design improvements and innumerable valve types have been introduced in recent years. The wide selection of modern valve types (see Figure 14) provides the following advantages:

1. Throughputs and efficiencies can be as high as sieve or bubble cap trays.
2. Very high flexibility can be achieved and turndown ratios of 4 to 1 are easily obtained without having to resort to large pressure drops at the high end of the operating range.
3. Special valve designs with venturi-shaped orifices are available for duties involving low pressure drops.
4. Although slightly more expensive than sieve trays, valve trays are very economical in view of their operating superiority.
5. Since an operating valve is continuously in movement, the valve tray can be used for light-to-moderate fouling duties. APV has successfully used valve trays with brewery effluents containing waste beer, yeast, and other materials with fouling tendencies.

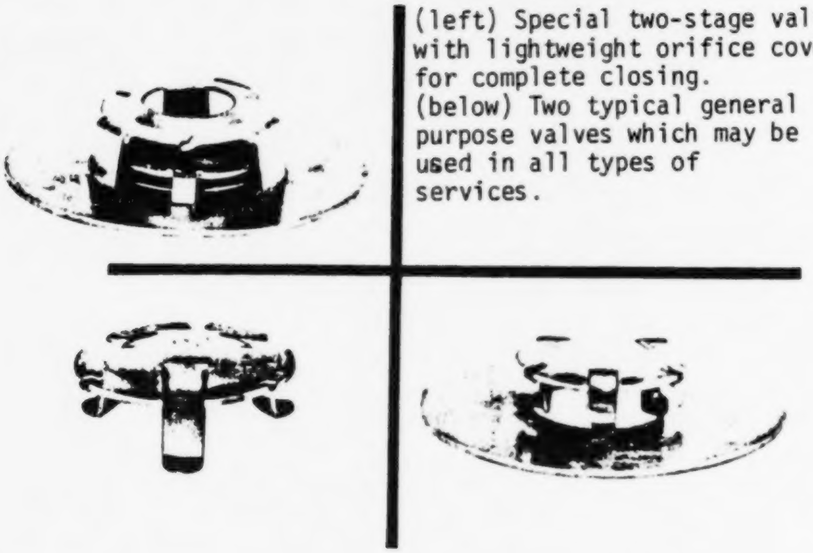
Bubble Cap Tray--Although many bubble cap columns (Figure 13) still are in operation, bubble cap trays rarely are specified today because of high cost factors and the excellent performance of the modern valve-type tray. The bubble cap, however, does have a good turndown ratio and is suitable for low liquid loadings.

Baffle Tray--The liquid flows down the baffle tray column by splashing from one baffle to the next lower baffle. The gas or vapor rises through this curtain of liquid spray.

Although the baffle type tray has a relatively low efficiency, it can be useful in treating waste flows when the liquid contains a high fraction of solids (see Figure 14).

Packings--

Packing is the most economical method of contacting liquid and gas streams in distillation columns, particularly small diameter columns. Most packings can be purchased from stock on a cubic-foot basis. In addition, the mechanical design and fabrication of a packed column is quite simple (see Figure 15). Packing is limited in waste treatment functions because of the tendency to foul and, in APV experience, because of less predictive performance at low liquid loads or high column diameters because of liquid distribution problems.



(left) Special two-stage valve with lightweight orifice cover for complete closing.
(below) Two typical general purpose valves which may be used in all types of services.

Figure 14. Typical valves used in valve tray columns.

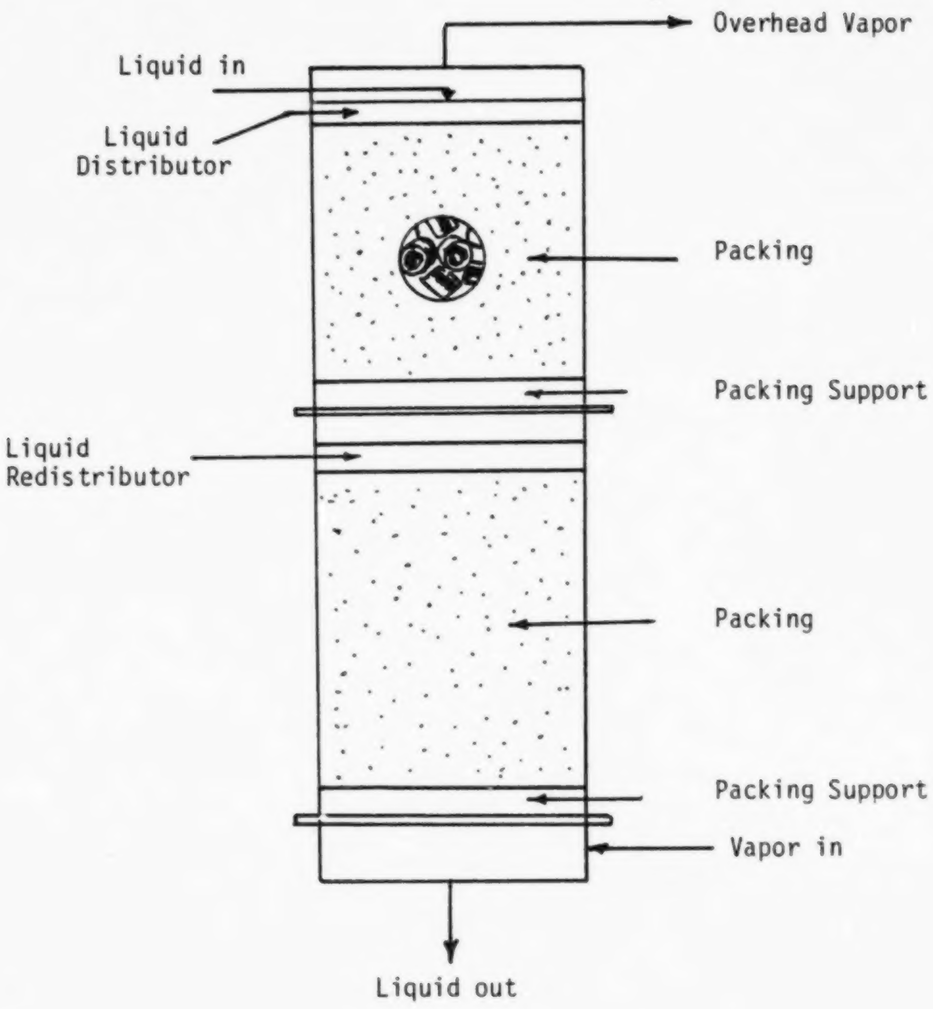

Overhead Vapor
Liquid in
Liquid Distributor
Packing
Packing Support
Liquid Redistributor
Packing
Packing Support
Vapor in
Liquid out

Figure 15. Illustration of packed column internals.

The most widely used packings are randomly-dumped packings such as Rashig rings, Pall rings, and ceramic saddles (Figure 16). These are available in various plastics, a number of different metals, and, with the exception of Pall rings, in ceramic materials. While plastic packings have the advantage of corrosion resistance, the self-wetting ability of some plastic packings (such as those made of fluorocarbon polymers) sometimes is poor, particularly in aqueous systems. This considerably increases the height equivalent of a theoretical plate (HETP) as compared with equivalent ceramic packagings.

High-efficiency metal mesh packings have found increasing favor in industry during recent years. One type uses a woven wire mesh that becomes self-wetting because of capillary forces. This helps establish good liquid distribution as the liquid flows through the packing geometry in a zig-zag pattern. If properly used, high-efficiency structured packings can provide HETP values in the range of 15 to 30 cm (6 to 12 inches). This can reduce column heights, especially when a large number of trays is required. Such packings, however, are very expensive and each application must be studied in great detail.

With both random and high-efficiency structured packings, considerable attention must be given to correct liquid distribution. Certain types of high-efficiency packing are extremely sensitive to liquid distribution and should not be used in columns over 2 feet (0.6 m) in diameter. Positioning of these devices and the design of liquid distribution and redistribution are important factors that should be determined only by experts.

Instrumentation

One of the most important requirements of any distillation system is the ability to maintain the correct overhead and bottoms compositions from the column by means of proper controls and instrumentation. While manual controls can be supplied, this approach rarely is used today in the United States. Manual control involves the extensive use of rotameters and thermometers which, in turn, involves high labor costs, possible energy inefficiency, and, at times, poor quality control. Far better control is obtained through the use of pneumatic or electronic control systems.

Pnuematic Control Systems--

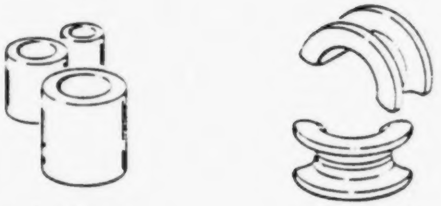
The most common form of distillation column instrumentation is the pneumatic-type analog control system. Pneumatic instruments have the advantage of being less expensive than other types, and since there are no electrical signals required, there is no risk of an electrical spark. One disadvantage is the need to ensure that the air supply has a very low dew point (usually -40°C (-40°F)) to prevent condensation in the loops.

Electronic Control Systems--

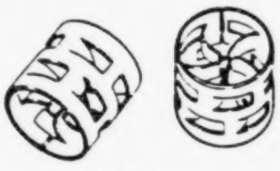
Essentially, there are three types of electronic control systems:

1. Conventional electronic instruments,

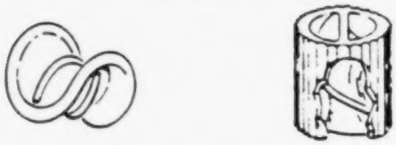
2. Electronic systems with all explosion-proof field devices,



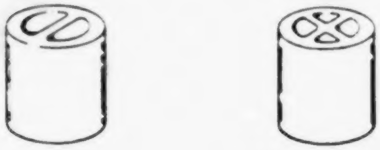
(a) Raschig rings (b) Intalox saddle



(c) Pall rings



(e) Berl saddle (d) Cyclohelix spiral ring



(f) Lessing ring (g) Cross-partition ring

Figure 16. Types of packing typically utilized in packed columns.

3. Intrinsically safe electronic systems.

A clear understanding of the differences between these electronic control systems is important.

Most distillation duties involve at least one flammable liquid which is being processed in both the vapor and liquid phases. Since there always is the possibility of a leak of liquid or vapor, particularly from pump seals, it is essential for complete safety that there be no source of ignition in the vicinity of the equipment. While many instruments such as controllers and alarms can be located in a control room removed from the process, all local electronic instruments must be either explosion proof or intrinsically safe.

With explosion-proof equipment, electrical devices and wiring are protected by boxes or conduit that will contain any explosion that may occur. In the case of intrinsically safe equipment, barriers limit the transmission of electrical energy to such a low level that it is not possible to generate a spark. Since explosion-proof boxes and conduits are not required, wiring costs are reduced.

For any intrinsically safe system to be accepted for insurance purposes, Factory Manual (FM) or Canadian Standards Association (CSA) approval usually must be obtained. This approval applies to a combination of barriers and field devices. Therefore, when a loop incorporates such instruments from different manufacturers, it is essential to ensure that approval has been obtained for the combination of instruments.

Reboiler

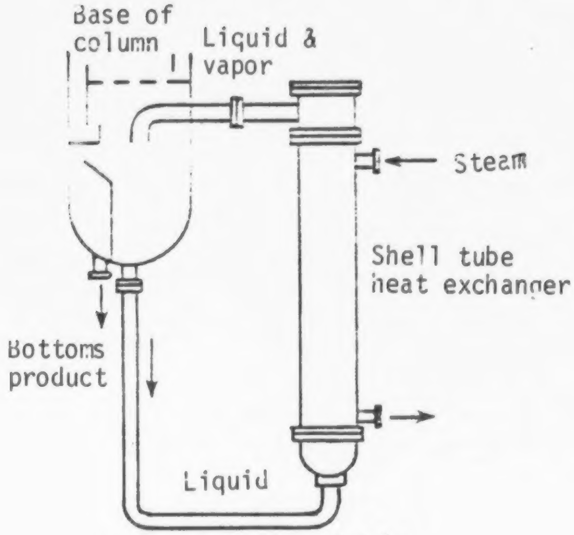
Although there are many types of reboilers, the shell and tube thermosyphon reboiler is used most frequently. Boiling within the vertical tubes of the exchanger produces liquid circulation and eliminates the need for a pump. A typical arrangement is shown in Figure 17.

For certain duties, particularly when the bottoms liquid has a tendency to foul heat transfer surfaces, it is desirable to pump the liquid around the heat exchanger. Since boiling can be suppressed by use of an orifice plate at the outlet of the unit, fouling is reduced. The liquid being pumped is heated under pressure and then is flashed into the base of the column where vapor is generated.

An alternative approach is the use of a plate heat exchanger as a forced circulation reboiler (Figure 18). With this technique, the very high liquid turbulent flow induced within the heat exchanger through the use of multiple corrugated plates holds fouling to a minimum. Meanwhile, the superior rates of heat transfer that are achieved reduce the surface area required for the reboiler.

Condensers

Since most distillation column condensers are of shell-and-tube design, the design engineer has the option of condensing on either the shell or tube


Base of column
Liquid & vapor
Steam
Shell tube heat exchanger
Bottoms product
Liquid

Typical shell and tube thermosyphon reboiler arrangement

Figure 17. Shell and tube reboiler.

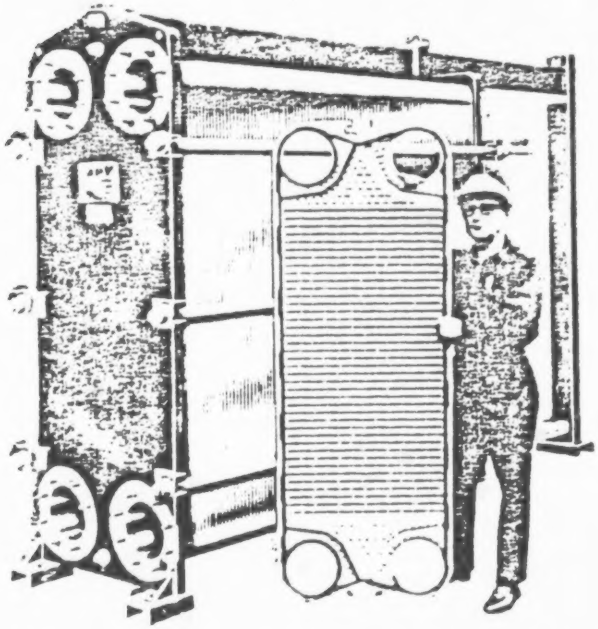


Figure 18. Plate heat exchanger reboiler.

side. From the process point of view, condensation on the shell side is preferred since there is less subcooling of condensate and a lower pressure drop is required. These are important factors in vacuum duties. Furthermore, with cooling water on the tube side, any fouling can be removed more easily.

Tube-side condensation, on the other hand, can be more advantageous whenever process fluid characteristics dictate the use of more expensive, exotic materials. Capital costs of the unit then may be cut by using a carbon steel shell.

Preheaters/Coolers

The corrosion characteristics of the waste stream dictate the selection of plate or shell-and-tube preheaters and product coolers. If the VOCs do not excessively degrade or swell gasket materials, a plate heat exchanger is an extremely efficient preheater. Heat can be transferred from the tops and bottoms products for this purpose. The plate heat exchanger can be easily disassembled for cleaning. Heat transfer to aromatic VOCs such as benzene and toluene normally is accomplished in a series of tubular exchangers.

Vent Condenser

It is normal practice in some distillation systems to use a vent condenser after the main condenser to serve as an air pollution control system. Usually of the shell-and-tube type, the vent condenser will typically have 1/10 the area of the main unit. Chilled water is used to cool the noncondensible gases to about 7-10°C (45-50°F), although some plants use process cooling water as a "back-up" system.

Pumps

Distillation is used to process many VOC fluids that are highly flammable. It is desirable that explosion-proof (Class 1, Group D, Division 1) pump motors be used. Centrifugal pumps are reliable and can economically provide the required flow capacities and operating pressures. The bottoms product of the distillation unit or the reboiler may, however, contain particulate material necessitating the use of positive displacement pumps.

EQUIPMENT AND SYSTEM SUPPLIERS

A number of companies manufacture distillation equipment and provide complete package units for specific applications. Most distillation systems are custom designed because of the large number of variable process factors that must be taken into consideration. These companies usually have computer capability for complete system design as well as pilot plant facilities of varying capability.

Most companies also provide complex distillation systems which include multicomponent units. In these, solvent extraction, carbon adsorption, and distillation processes may be integrated in solvent recovery or stream purification operations.

In most cases, complete package systems can be provided in preassembled modular or skid-mounted units. This will usually result in significant overall installation cost and time reductions.

Some of the major suppliers for distillation systems used in solvent recovery and VOC removal operations are listed below:

- APV Equipment, Inc.--pilot plant facilities for evaporation.
- Aqua-Chem, Inc.--pilot plant facilities for evaporation.
- Artisan Industries, Inc.--pilot plant facilities for distillation, solvent extraction.
- Chem-Pro Corp.--pilot plant facilities for distillation, stripping, extraction.
- DCI Corp.--provides standard package systems for distillation and live steam stripping.
- Glitsch, Inc.--pilot plant facilities for distillation, scrubbing, stripping, extraction.
- The Pfaudler Company--pilot plant facilities for distillation.
- Vara International, Inc.--experts primarily in integrated adsorption/distillation systems for solvent recovery from gas streams.

This is only a representative list of equipment suppliers and is not intended to be a complete listing of all companies providing equipment or systems. The locations of the companies are presented in Table 16.

COST

Capital Cost

The cost of a distillation system is dependent upon such design variables as the size and type of reboiler, column height, column diameter, column internals, degree of automation, and materials of construction. These design considerations must be determined for the feed stream to be processed and the component separation which is required. Changes in component relative volatilities, feed rates, and required product purities can effect large differences in system costs.

Equipment installation costs vary with the type and size of equipment, the geographical location, and the site characteristics. Peters and Timmerhaus (1968) present a general range of installation costs as a percentage of the purchased-equipment cost for various types of equipment. Taking into consideration the major equipment components of a distillation system, an installation cost of 25-50 percent of the equipment cost would be

TABLE 16. REPRESENTATIVE LIST OF DISTILLATION SYSTEM SUPPLIERS

APV Equipment, Inc.	Tonawanda, NY
Aqua-Chem, Inc.	Milwaukee, WI
Artisan Industries, Inc.	Waltham, MA
Chem-Pro Corporation	Fairfield, NJ
DCI Corporation	Columbus, OH
Glitsch, Inc.	Dallas, TX
The Pfauldler Company	Rochester, NY
Vara International	Vero Beach, FL

indicated. However, APV Distillation Handbook refers to a typical installed system cost as being 1-1/2 to 2 times the equipment cost.

Custom-built, preassembled process systems or process modules is an option being offered by most system suppliers and is claimed to provide significant savings in cost and time. An overall cost savings of 25-40 percent for a preassembled unit is projected in Chemical Processes Brochure, p. 200, and the reduction in manhours and time length for the project are depicted graphically in Figures 19, 20, and 21.

In one APV Equipment, Inc., distillation system application (described in APV Distillation Handbook with supplemental information via telephone conversation with Dr. Cooper, APV), ethanol is recovered from an aqueous waste stream containing about 3-percent ethanol in addition to suspended sludge and yeast solids. One major problem is that the liquid tends to foul heat transfer surfaces. A paraflow plate (corrugated plate) heat exchanger reboiler, which is less susceptible to fouling than many other types of heat transfer equipment, is utilized to minimize this problem. The plate corrugations enhance the liquid turbulence, which assists in shearing the fouling deposits off the surface. In addition, the paraflow design is easily cleaned in place and can be readily opened if fouling becomes excessive. The efficiency of the column trays, however, has not been affected by the fouling tendency of the liquid. APV attributes this primarily to the use of valve trays as the gas-liquid contacting device. The small valves in the holes on the trays are continually moving up and down and there is some rotation, thus helping to prevent buildup of foulant in the area around the holes. The system performance and cost are illustrated by the following process information:

Feed rate	265 L/min (70 gal/min)
Feed temperature	100°C (211°F)
Ethanol concentration (feed)	3 percent v/v
Ethanol concentration (distillate)	95 percent v/v
Ethanol concentration (bottoms)	<0.02 percent v/v
System equipment cost (1-1/2 times equipment cost assumed)	$1,050,000
Annualized system equipment cost (10 years, 10-percent interest)	$171,000

The bottoms product containing water, solids, and no more than 0.02 percent v/v alcohol, can be readily utilized in related plant byproduct processes.

Operating Costs

The total operating costs will vary significantly from a small batch distillation system to a very high throughput continuous process. The total

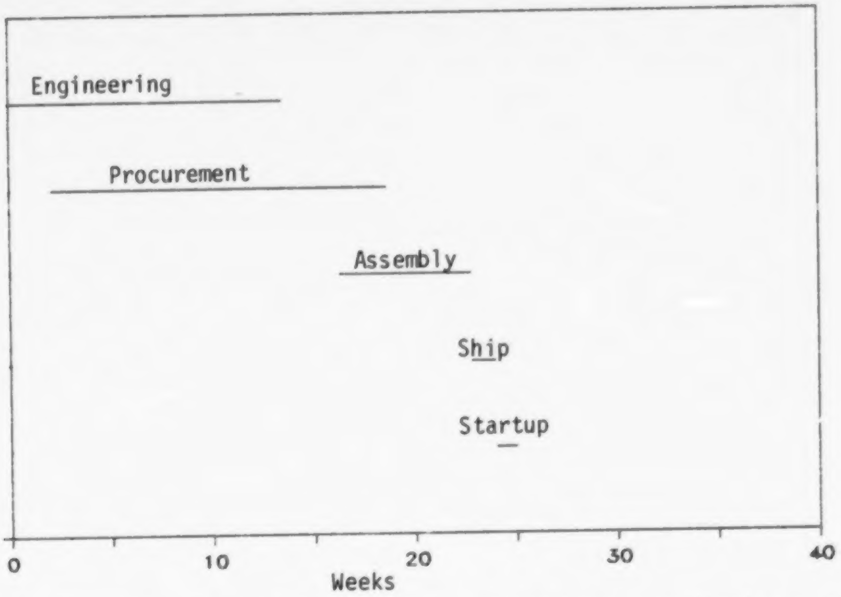


Figure 19. Time schedule for Chem-Pro preassembled distillation units (Chem-Pro, 1985)

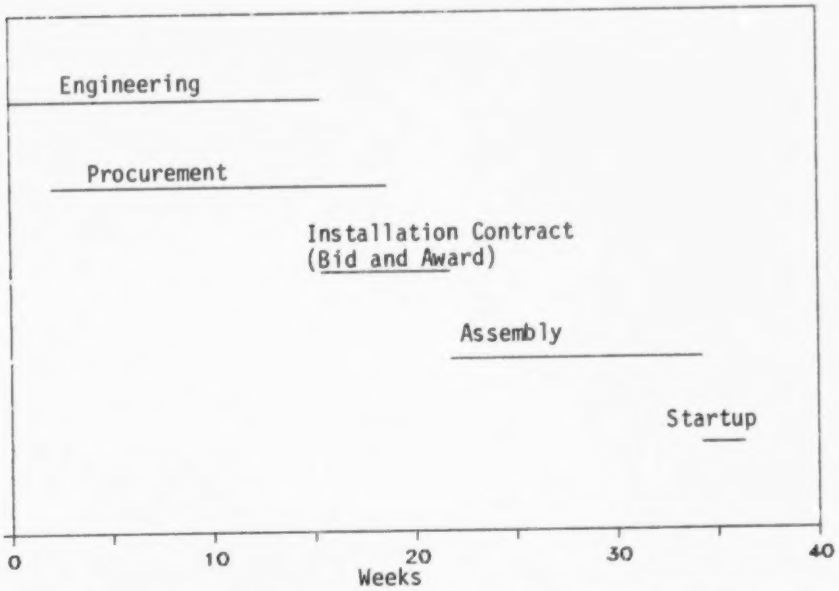


Figure 20. Time schedule for Chem-Pro field-erected distillation units. (Chem-Pro, 1985)

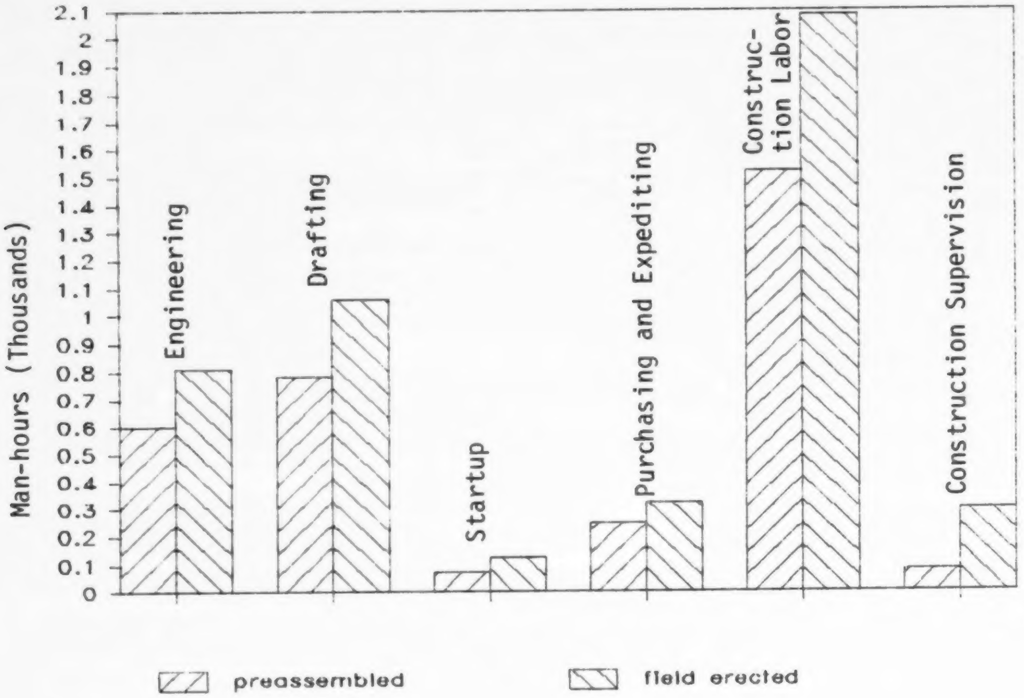


Figure 21. Labor comparison of Chem-Pro preassambled and field erected distillation units (Chem-Pro, 1985).

cost for processing a large feed volume will be much greater than for the smaller operation, due primarily to the much greater steam usage. On a unit cost basis, however, the steam usage becomes the predominant variable cost as the feed volume becomes large, and other costs such as labor and maintenance become less significant. In a small batch operation that may require considerable operator attention, the unit labor cost can be fairly significant (due to low volume, high labor) while steam usage would be equivalent on a unit cost basis to a high-volume process.

In the case of the APV system described in the previous section, the operating cost may be determined if some basic assumptions are made. The following shows the results of the calculation procedure along with the assumptions employed:

Operating Conditions

Feed rate	160 L/min (7 gal/min)
Operating hr/year	8,400 hr
Ethanol concentration (feed)	3 percent
Ethanol concentration (distillate)	95 percent
Ethanol concentration (bottoms)	0.02 percent maximum
Steam rate, per lb effluent processed (APV Distillation Handbook, typical for dilute alcohol streams)	0.09 L (0.2 lb)

Operating Costs

1. Annual

Steam	$ 58,000
Cooling water and electrical (10 percent of steam)	5,800
Operator (0.25 operators at $15/hr)	31,500
Maintenance (10 percent of equipment cost)	70,000
Total operating costs	$165,300

2. Unit Volume

Effluent processed	$0.025/L ($0.0065/gal)
Ethanol recovered	$0.177/L ($0.216/gal)

Total Cost

1. Annual

Operating cost	$165,300
Depreciation and interest	171,000
Total cost	$336,300

2. Unit Volume

Effluent processed	$0.035/L ($0.0093/gal)
Ethanol recovered	$1.18/L ($0.311/gal)
	$1.475/mg ethanol recovered

SOURCES OF EMISSIONS TO THE ENVIRONMENT

The potential for VOC emissions to the air from distillation processes would include losses via condenser vents, accumulator tank vents, and storage tank vents.

Emissions from the condenser vent should be primarily noncondensible gases. However, if the condenser should become overloaded for any reason, VOC emissions to the air could become significant. A vent condenser may be used after the main condenser in order to minimize the amount of volatiles emitted.

Emissions from operating and storage tanks would be displacement losses of equilibrium vapor from the liquid holdup.

APPLICATIONS TO PRETREATMENT

Distillation is applicable to the pretreatment of hazardous waste to remove VOCs, either as a primary treatment or in conjunction with solids separation in a thin-film evaporator. Solids should be removed from the waste stream, either by decanting the liquid from a settler or by processing the waste in a thin-film evaporator. Solids which remain in the waste in the distillation column can foul the plates and require process downtime for cleaning, as well as reducing column efficiency. The distillation column can be directly connected to the thin-film evaporator so that the vapors from the evaporator are then fed to the column.

Distillation serves to separate VOC components from each other, VOCs from oils, or VOCs from water. The separation of components serves to increase the value of the organic phase, to improve the energy content of a waste, or to separate components that cannot be easily separated by a thin-film evaporator or a steam stripper.

Multiple distillation columns are used at TSDFs to provide flexibility for various types of separations that a TSDF may require. Wastes vary in volume, the number of trays needed for separation, and in the reflux ratios needed for separation of the components. The design of the distillation columns at a TSDF generally should focus more on flexibility of operation rather than optimum design for a specific application.

Distillation by batches is commonly carried out at TSDFs to treat batches of the waste which are collected. Continuous distillation is more appropriate for large volumes of waste generated continuously, which is not variable with time.

Distillation as a pretreatment process for removal of VOCs from hazardous waste streams would have potential application in processing (1) liquid organic wastes and (2) aqueous organic waste streams. In the case of liquid organic wastes, a product reclamation value would be necessary in order to justify the cost of distillation. With no appreciable recovery value, other treatment methods such as waste heat recovery or incineration would likely prove more economical. Distillation is currently widely used for solvent recovery from organic waste streams at commercial and industrial treatment, storage, and disposal facilities (TSDFs). The processes may or may not use rectification depending upon the waste stream composition and the desired degree of purity of the recovered product. Distillation of organic waste streams usually results in a bottoms residue consisting of sludge or heavy organics for which there is no use. The most common means of disposal for these residues is as fuel in cement kilns. In some cases, distillation bottoms are landfilled.

Distillation of aqueous organic streams may be feasible when an organic compound is present in concentrations that would result in an appreciable recovery value or where the combination of organic recovery and wastewater purification is of significant value. The organic compound would normally be more volatile than water for distillation to be considered for such applications. For VOC removal from an aqueous stream, great care is normally taken to ensure that the aqueous phase has been stripped to a very low VOC concentration (less than 0.1 percent) to facilitate disposal of the water. The aqueous phase is often acceptable for disposal in a municipal wastewater treatment facility if low concentrations of residual organics can be obtained. Otherwise, the aqueous residue would require disposal in evaporation ponds or landfarms.

SECTION 7

FIELD TEST RESULTS: THIN-FILM EVAPORATORS

Thin-film evaporators were investigated at three hazardous waste recycling plant sites: Plant A, Plant B, and Plant C. At Plant A, a high-boiling organic was separated from a waste (together with a few percent VOC). At Plant B, there was a mixture of VOCs being recovered from a waste, with a range of VOC volatility. At Plant C, a highly volatile VOC (acetone) was recovered from a waste. Plants A and B were operating under vacuum, and Plant C was at atmospheric pressure. Thin-film evaporators typically only have a few minutes residence time for the waste material in the evaporator, and grab samples of the feed, bottoms, and product are believed to characterize the process during the time that the samples are taken. Thin-film evaporators are described in Section 5 of this report.

Thin-film evaporators are used in many solvent recovery operations. Typically, 80 percent of the volatile materials can be recovered, with a sludge containing residual VOC obtained at the bottom of the evaporator.

THIN-FILM EVAPORATOR FIELD EVALUATION AT PLANT A

A 1-day site visit was conducted at Plant A in order to collect information on engineering design and cost, along with selected process samples (Allen, 1984a). The primary activity at Plant A is the recovery of organic wastes and contaminated chemicals. The company also engages, to a lesser extent, in waste management for some firms.

The recovery and purification processes involve three VOC recovery systems:

1. One Luwa thin-film evaporator;
2. One batch fractionation distillation column;
3. One continuous feed fractionation distillation column.

Support facilities include a concrete drum storage and management area, a cooling water system, an activated sludge wastewater treatment system, an oil-fired boiler system for steam generation, and a main building providing housing for offices, laboratories, and locker rooms.

Process Description

The Luwa thin-film evaporator processes organic wastes from the furniture, chemical, dry cleaning, and paint industries. Wastes processed include furniture finishing wastes and other organic wastes which could contain sludges. The sludge would include paint films, particulates, and insoluble organic materials.

The major requirement for processing in the Luwa still is that the still bottoms are acceptable for incinerators. This means that the bottoms must have an energy content greater than 38,000 kJ/L (100,000 Btu/gal), contain less than 1-percent chlorides, and be suitable for pumping. The process economics require that typically greater than 60 percent of the waste be recovered as volatiles from the still overheads.

There were no apparent mechanical safety problems associated with the Luwa still, apart from the moving drive belt on the still rotor.

Waste and contaminated solvents and organic byproducts are received at the site in drums and bulk shipments. Extensive laboratory analyses are performed in order to ensure consistency with the manifest identification. The standard operation is to process each batch of chemicals through the Luwa Evaporator during which 70 to 95 percent of the material is stripped off as overhead product. The amount stripped off is selected so that the bottoms product is acceptable in heat value and viscosity for offsite consumption as fuel. The overhead product may or may not be further refined through fractionation distillation, depending upon the intended end-use. Distillation bottoms are shipped offsite and utilized as fuel in cement and expanded aggregate kilns.

The Luwa Thin-Film Evaporator System at Plant A consists of a 4.0 m^2 (43 ft^2) heat transfer surface Luwa Evaporator, entrainment separator, condenser, feed pump, bottoms pump, distillate pump, vacuum system, and instrumentation (Figure 22). Steam or sometimes hot oil is used as the heating medium. Steam is typically controlled at about 38°C (100°F) above the boiling point of the distillate. Evaporator feed rate and system pressure (vacuum) control are determined based on the material being processed. A typical feed rate is 23 L/min (6 gpm), but may be set over a range of from 4 to 45 L/min (1 to 12 gpm). The cooling water for the overhead product condenser is generally maintained in the range of 10 to 16°C (50 to 60°F), with a flow rate of about 1,500 L/min (400 gpm). The system is operated under reduced pressure with either of two vacuum pump systems, a Kinney or Nash, being utilized. The two Kinney pumps at Plant A are positive displacement oil-sealed units which can be used to obtain operating pressures down to about 50 mm Hg absolute (28 inches Hg vacuum). The single Nash pump is a water-sealed displacement pump which can obtain operating pressures of about 350 mm Hg absolute (16 inches Hg vacuum).

The most persistent maintenance problem involves the bottom rotor shaft bearing. It is estimated that this bearing is replaced about eight times per year with a downtime of 6 hours per occurrence. A maintenance overhaul is performed every 4 or 5 years during which time the rotor edges are redressed.

Process Effectiveness

Based on discussions with Plant A personnel and the engineering judgment of the authors, the thin-film evaporator at Plant A can be used in the following applications:

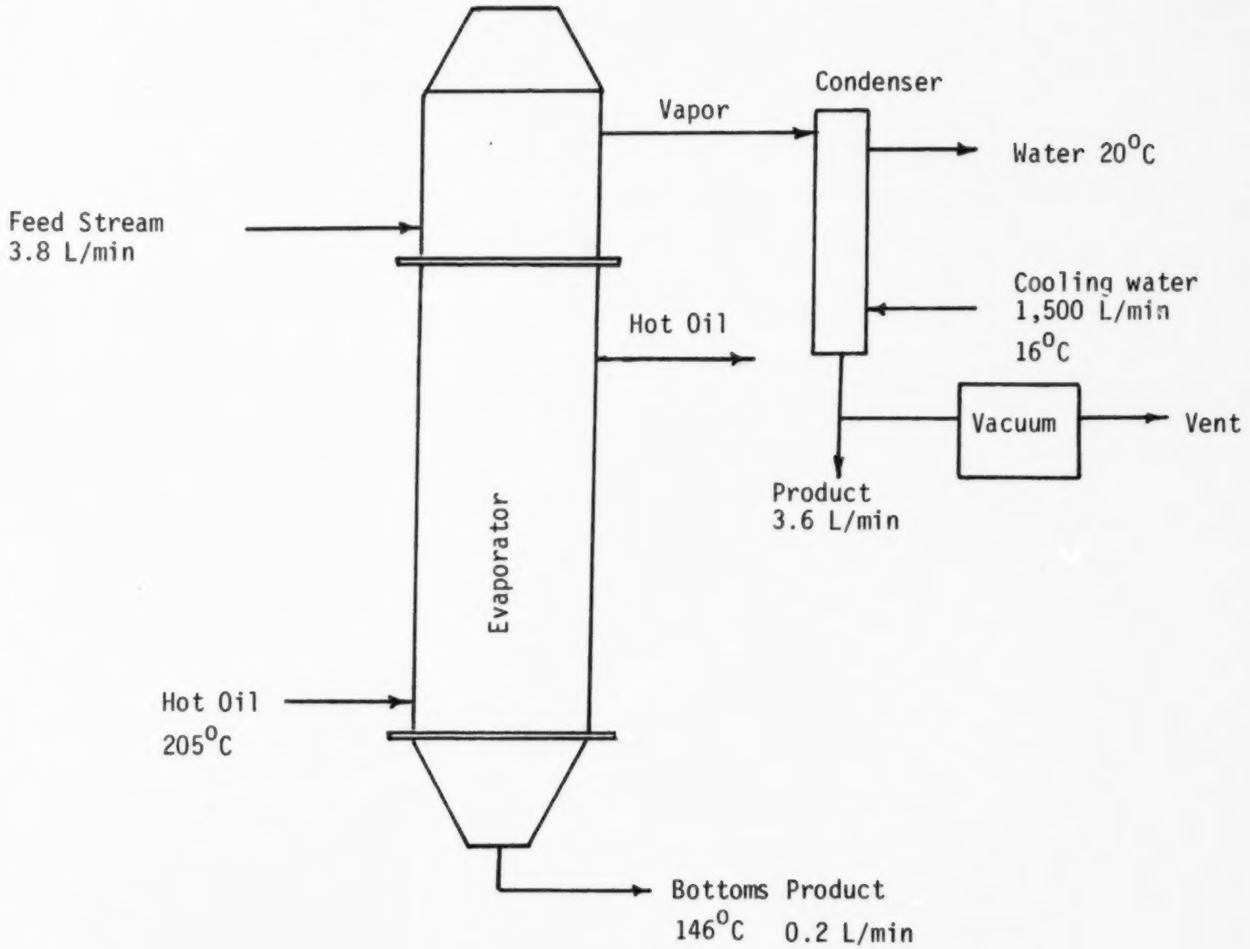

Feed Stream
3.8 L/min
Hot Oil
205°C
Evaporator
Vapor
Hot Oil
Condenser
Water 20°C
Cooling water
1,500 L/min
16°C
Vacuum
Vent
Product
3.6 L/min
Bottoms Product
146°C 0.2 L/min

Figure 22. Solvent recovery: Mixed chlorinated xylenes.

1. Removal of VOCs from organic streams which may contain viscous high molecular weight organics or solids.

2. Removal of VOCs from sludges such as insoluble organics and particulate solids.

3. Concentration of aqueous sludges such as insoluble organics and particulate solids.

4. Removal of VOCs from aqueous streams where the VOC volatility is higher than that of water.

5. Removal of water from streams containing relatively high concentrations of volatile organics of lower volatility than water (water removed as overhead product).

During the visit to Plant A, a "batch" consisting of mixed chlorinated xylenes was being processed through the thin film evaporator (Allen, 1984a). This waste treated at Plant A represents a class of waste oils containing a small amount of solids and approximately 5-percent VOCs. Since this material contained few solids, approximately 95 percent of the feed was being taken overhead, with bottoms being acceptable for fuel. The purpose of the treatment was to recover the chlorinated xylenes.

The data obtained from samples of the feed, the bottoms, and the product shortly after process startup are presented in Table 17. The headspace analysis demonstrated that the volatile organic material was removed by the Luwa still from the bottoms. The following removal effectiveness was estimated (based upon a material balance using the headspace analysis and 95-percent product recovery, Appendix F):

Methylene chloride	99.91
Chloroform	>99.99
1,1,1-Trichloroethane	>99.5
Toluene	95.4
Freon TF	80.0

Based on headspace analysis, the concentrations of the volatiles appear to be reduced in the bottoms of the thin-film evaporators. The vapor pressures of the more volatile compounds are reduced more than 90 percent by the treatment.

Process Residuals

There are several potential VOC fugitive emission sources associated with the operation of the Luwa still. Storage tank emissions are possible to a limited extent. (The feed tank was covered during the test visit.) Leaks from the transfer lines are possible, together with any potential spills of materials. The vacuum pumps remove the vapors from the condenser and the vented vapors are an air emission source. The air emissions from the vacuum pump system are expected to be relatively low during the normal operation of the system, but would be much greater if the condenser were unable to condense some of the vapors, if air was leaking into the system, or if the still were

TABLE 17. PLANT A THIN-FILM EVAPORATOR WASTE COMPOSITIONS AND HEADSPACE ANALYSIS

	Feed		Product		Bottoms[a]
	Liquid composition (vol. %)	Headspace analysis[b] (mg/L)	Liquid composition (vol. %)	Headspace analysis[b] (mg/L)	Headspace analysis[b] (mg/L)
Methylene chloride	2.0	1.7	0.9	0.97	0.03
Chloroform	1.5	5.1	ND	0.14	<0.01
1,1,1-trichloroethane	0.7	0.11	ND	0.14	<0.01
Toluene	1.3	>0.01	1.6	0.04	0.03
Mixture of high boiling hydrocarbons	94.4	ND	93.9	ND	ND
Freon TF	ND	0.06	1.8	1.5	0.24

ND = not detected.

[a] Bottoms solid upon cooling and no solids analysis was performed.

[b] at 25°C.

TABLE 18. PLANT A VACUUM PUMP VENT GAS ANALYSIS

	Process vent 10 minutes[a] (mg/L)	Process vent 5 minutes[a] (mg/L)	Duplicate Process vent 5 minutes[a] (mg/L)	Field blanks 1	Field blanks 2
Chloroform	2.4	17.8	6.1	-	-
1,1,1-Trichloroethane	3.1	3.05	2.35	-	-
Trichloroethylene	0.87	0.59	0.61	-	-
Tetrachloroethylene	1.0	1.04	1.01	-	-
Toluene	27.1	23.5	25.8	-	-
Ethyl benzene	0.31	0.52	0.45	-	-
Xylenes	1.41	2.16	1.9	0.1	-

[a] Sample period.

operating with an overhead rate that was greater than the condenser could handle. When a new waste type is introduced into the still, the bottoms are collected in an open 50-gallon drum for part of the run. These bottoms are hot and are a fugitive emission source.

The Nash water ring seal vacuum pump will absorb some of the VOCs in the condenser gas into the water. A stream of the water containing VOCs would be transferred to water treatment. The still bottoms are incinerated and the condensate is either sold as a product or is processed further at the plant.

The volatile materials, methylene chloride and chloroform, were present in the feed stream at somewhat higher concentrations than in the product, and were not present to a significant extent in the bottoms. This suggests a possible loss of some of the more volatile materials to the atmosphere through the vacuum pump vent. The exhaust of the vacuum pump did contain some volatile materials during startup. The following removal effectiveness was estimated using a material balance from the information presented in Table 17 (based upon the headspace analysis and 95-percent recovery), according to boiling point:

	Estimated Removal Effectiveness
Methylene chloride (b.p. = 40.7°C)	55%
Chloroform (61.3°C)	97%
1,1,1-Trichloroethane (74°C)	-21%
Toluene (110°C)	-17%

A negative sign indicates a VOC recovery above 95 percent during processing. Although there is an expected error of 15 percent or less in the data, and even greater error in differences and estimates based on gas partitioning, the data do suggest that the lower boiling VOCs may be subject to much higher process losses than higher boiling VOCs. In addition, the vent losses are expected to be higher upon startup.

Carbon adsorption tubes were analyzed for VOCs. Five tubes were analyzed, one 10-minute sample (85 mL/min), two 5-minute samples, and two field blanks. The analysis of the gas samples of the vacuum pump discharge vent is presented in Table 18. Chloroform and 1,1,1-trichloroethane were present in the vent discharge with statistically significant quantities of the higher boiling VOCs (toluene, ethyl benzene, xylene). The absence of methylene chloride captured on the carbon tube and the apparent insensitivity of the quantity of chloroform captured to the length of sampling time suggest that the quantities of the more volatile chlorinated compounds may be greater than reported in Table 18.

These data suggest that Luwa stills operating under a vacuum can have potentially significant VOC emissions. The emission rate would depend on the operating conditions of the still. The data reported in Tables 17 and 18 were taken during startup and the concentrations observed were expected to be lower after the transitional period of startup.

Process Cost

The equipment at Plant A was purchased second-hand and, therefore, capital costs must be estimated for a replacement system. This estimate is provided in Table 19. The estimate does not include cost of a steam boiler.

Table 20 provides cost estimates of the thin-film evaporator at Plant A. The typical unit costs for operating this process were 0.0279 \$/L waste treated and 0.033 \$/L (41.1 \$/Mg) of VOC removed as shown in Table 20.

THIN FILM EVAPORATOR FIELD EVALUATION AT PLANT B

Process Description

The primary activity at Plant B is the reclamation of contaminated solvents and other chemicals through evaporation and distillation. About 10 percent of the incoming chemicals are contaminated products with the remainder being classified as hazardous waste. Approximately 85 percent of the reclaimed chemicals are recycled back to the generator with the remainder being marketed to suitable end users.

Processing equipment include two Votator agitated thin-film evaporators, two distillation reboilers, eight fractionation columns, and one caustic drying tower. Support facilities include 97 storage tanks (one-million-gallon capacity); two warehouses containing dyked concrete pads for drum storage; an analytical laboratory; gas-fired steam generation; and an office building. A fleet of tractors and vacuum tankers is maintained for transporting solvents and chemicals to and from the plant.

The wastes processed by Plant B are from the chemical, paint, ink, recording tape, adhesive film, automotive, airlines, shipping, electronic, iron and steel, fiberglass, and pharmaceutical industries. The types of chemicals recovered include the following VOCs: alcohols, ketones, esters, glycols, ethers, chlorinated solvents, aromatic hydrocarbons, petroleum naphthas, freons, and specialty solvents. Contaminated organic chemicals and solvents are received in bulk and drum shipments and processed for reclamation and recycle.

Plant B is able to remove the VOCs from still bottoms, coating residues, obsolete paints, and inks using thin-film evaporators.

All waste material is either processed first in the thin-film evaporator or the distillation reboilers. Approximately 90 percent of the incoming shipments are processed through one of two Votator thin-film evaporators during which about 80 percent of the material is stripped off as overhead product. The limiting factor for the amount of liquid which can be recovered is that the bottoms product must be acceptable in heat value and viscosity for offsite consumption as fuel. The overhead product may or may not be further refined through fractionation distillation, depending upon the intended end use. Thin film evaporator bottoms are shipped offsite and utilized as fuel in cement kilns.

TABLE 19. PLANT A REPLACEMENT CAPITAL COSTS (LUWA EVAPORATOR SYSTEM)[a]

Luwa Evaporator Model LN-0500[b]	$120,000
Main Auxiliaries (Condenser, Pumps, Vacuum System, Controls)	36,000
Piping, Fittings (materials only)	12,000
Structural Frame	6,000
Installation (Foundation, Erection, Piping, Wiring, Insulation)	120,000
Total Installed Cost	$294,000

[a] 1984 Cost (per Ray Danaher, LUWA Corp., July 23, 1984)

[b] 5.00 square meters (53.8 square feet)--4.00 square meters (43 square feet) model used at Plant A, no longer available.

TABLE 20. 1984 PLANT A OPERATING COST*

ANNUAL OPERATING COSTS	
Feed Rate	23 L/min (6 gpm)
Overhead Product, Percent of Feed	85 percent
Operating Labor	$10/hr, $66,000/yr
Maintenance Labor	$25,000/yr
Maintenance Materials	$9,000/yr
Laboratory (1.2 Analysts)	$24,000/yr
Fuel (Steam System, 19 L/hr [5 gal/hr])	$8/hr, $60,000/yr
Electrical (45 hp)	$1.70/hr, $11,000/yr
Cooling Water 1,500 L/min (400 gpm)	$4/hr, $26,000/yr
Overhead	$100,000/yr
Evaporator Bottoms Disposal ($0.05/L [$.22/gal])	$78,000/yr
Schedule Production	310 days/yr
Utilization (88 percent of schedule, 24 hr/day	273 days/yr
ANNUAL COSTS	
Annual Operating Cost	$217,200
Capital Recovery Factor (Avg. 10 yr at 10 percent	35,350
Total	$252,550
UNIT COSTS	
$/L waste treated	0.0279
$/L organic recovered (density = 0.8)	0.033
$/Mg organic recovered	41.1

[a] Based on information provided by Plant A for typical application. See Appendix F for details on calculations.

Each of two thin-film evaporator systems consists of a Votator thin-film evaporator, entrainment separator, condenser, feed pump, bottoms pump, distillate receiver and pump, and vacuum system. The two Votators are 4.65 m^2 (50 ft^2) and 5.76 m^2 (62 ft^2), respectively, in heating surface, steam heated, and generally operated under reduced pressure. The Votator has an external bottom rotor bearing which apparently works well and is relatively problem free. Plant B considers their operational experience with Votator evaporators to be very good with no major problems being experienced in about 2-1/2 years of service.

The following cases illustrate alternate treatment technologies at Plant B.

Case 1: A mixture of MEK and alcohol in water is fractionated by distillation. The distillation bottoms are predominantly water with most of the VOCs removed (99 to 98 percent removal).

Case 2: Water collects on the top of a separator tank when the waste is evaporated and condensed. The organic layer on the bottom is recovered.

Case 3: Water collects on the bottom of a separator tank, and a light hydrocarbon layer on the top is recovered.

Case 4: The waste is steam stripped. If alcohols are present, the partition of the alcohol is shifted to the xylene and toluene phase. The organic phase is recovered, and the water is left in the bottoms.

The Votator unit has the capability to run under vacuum so that lower processing temperatures can be used in the VOC recovery. Degradation reactions are also reduced by the design of the Votator, since there is an attempt to minimize the residence time of the feed.

Process Effectiveness

At the time of the visit, a batch consisting of isopropyl alcohol, xylene, and other VOCs was being processed through the 5.76 m^2 (62 ft^2) Votator (Figure 23). The reclaimable product was being stripped off overhead for further distillation and purification. The bottoms product was maintained at a concentration suitable for offsite fuel use.

The waste stream being processed with one pass under vacuum in the Votator contained isopropyl alcohol and xylene. Normally, two passes are used to process this material, with the more volatile IPA removed on the first pass and the less volatile xylene removed on the second pass. This two-pass technique would permit more effective capture and separation of the volatiles. On the batch sample, both IPA and xylene were being recovered on the same pass. The plant stated that vacuum would not be used normally for the recovery of VOCs from this waste stream and any vented VOCs would be expected to be emitted at a lower rate for the system under atmospheric pressure.

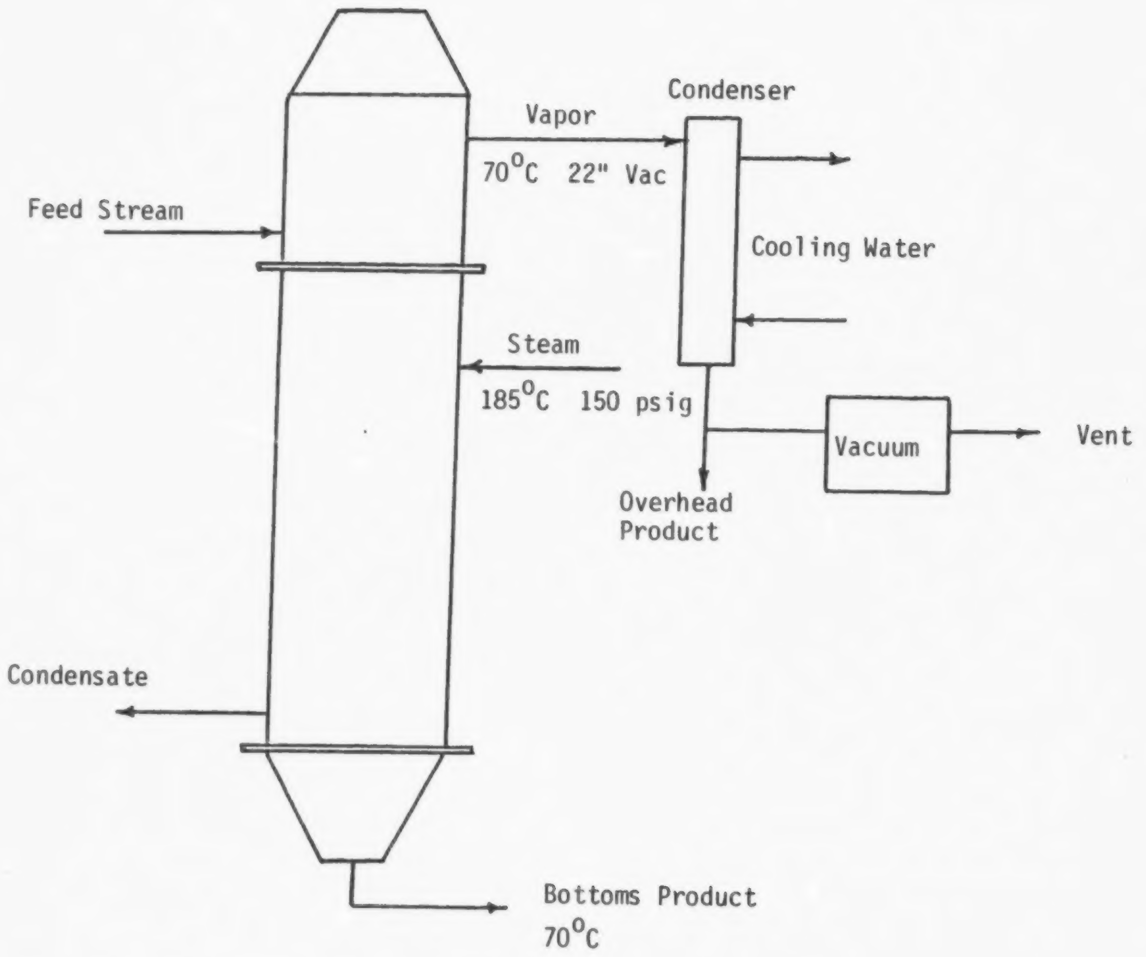

Feed Stream
Vapor
70°C 22" Vac
Condenser
Cooling Water
Steam
185°C 150 psig
Vacuum
Vent
Overhead Product
Condensate
Bottoms Product
70°C

Figure 23. Thin-film evaporation: Isopropanol, xylene recovery.

Samples were taken at the following points:

Feed stream,

Bottoms product,

Overhead product, and

Vacuum pump discharge (gas).

The analysis of the liquid samples is presented in Tables 21 and 22. The results from duplicate sampling and analysis is presented in the table. The vent gas analysis is presented in Table 23. The concentration of VOCs at equilibrium in the vapor phase is not substantially altered in the bottoms, although the volume of waste is reduced. For those vent gas components that could be correlated with the feed, the concentration of the VOC in the vacuum pump vent gas is approximately one-half the headspace concentration of the product.

The process parameters were:

Feed temperature: ambient,

System pressure: 5.5 kilopascal (22-inch vacuum),

Process Temperature: 70°C, and

Steam: 1 megapascal (150 psig).

Process Residuals

The sources of air emissions include storage tanks and the vacuum pump vent. The Votator system itself is not expected to contribute to air emissions from leaks, since any leaks would be into the system since it is under vacuum. Any such air leaking into the system would be removed by the vacuum pump along with some VOC vapors. The rate of venting from the vacuum pump is expected to be greater at the beginning of a process run, since there would be air at atmospheric pressure initially. The vent samples were taken at the same time that the liquid samples were taken after the process had stabilized.

The storage tanks were large, fixed roof tanks. The air emissions from these tanks would be expected to be working losses from the tank vents.

Process Cost

Specific, detailed operating and capital costs were not discussed primarily because of the relatively large number of, and differences in, process systems at this facility. In addition, the complexity of the process operations vary over a wide range, depending upon the particular feed stream being processed and the intended use of the product.

TABLE 21. ANALYSIS OF LIQUID SAMPLES, THIN FILM EVAPORATOR, PLANT B

	Feed		Product		Bottoms[a]
	Liquid composition (vol. %)	Headspace analysis[b] (mg/L)	Liquid composition (vol. %)	Headspace analysis[b] (mg/L)	Headspace analysis[b] (mg/L)
Isopropyl alcohol	38.2	0.75	42.9	0.69	1.6
Freon TF	0.6	38.	0.5	29.	5.3
Toluene	0.4	0.58	0.3	0.48	0.32
Ethyl benzene	11.4	5.5	10.4	10.4	9.0
Xylenes	49.2	22.	45.7	23.	39.0

[a] Bottoms solid upon cooling and were not analyzed as a liquid.

[b] at 25°C.

TABLE 22. ANALYSIS OF PRODUCT SAMPLES, THIN FILM EVAPORATOR, PLANT B

	Product sample		Duplicate product sample	
	Liquid composition (vol. %)	Headspace analysis[a] (mg/L)	Liquid composition (vol. %)	Headspace analysis[a] (mg/L)
Isopropyl alcohol	53.8	1.1	60.3	1.1
Freon TF	0.7	62.	0.6	51
Toluene	0.4	0.94	0.4	0.71
Ethyl benzene	8.4	5.3	7.0	4.8
Xylenes	34.0	19.	27.4	17.

[a] at 25°C.

TABLE 23. ANALYSIS OF GAS SAMPLES FROM PLANT B VACUUM CONDENSER VENT

	Vent sample (mg/L)	Vent sample (mg/L)
Unidentified (Freon TF?)[a]	10.24	32.4
Toluene	0.4	0.47
Ethyl benzene	2.3	2.1
Neohexane (Isopropanol?)[a]	2.23	5.7
Xylenes	6.8	6.21

[a] There were analytical problems identifying components.

Plant B stated that it would not be economical to fractionate waste streams with less than 6 to 8 percent reclaimable organics. Some order of magnitude costs provided were:

> \$0.26 per liter (\$1.00 per gallon) operating cost when organic is stripped as the overhead product.
>
> \$0.40 per liter (\$1.50 per gallon) operating cost where water is stripped overhead with the organic being the bottoms product.
>
> It is estimated that the installed cost of a new 5.76 m^2 (62 ft^2) Votator thin-film evaporator system would be about \$300,000.
>
> The cost of shipping the thin-film evaporator bottoms to a cement kiln are approximately \$0.05 to \$0.08 per liter (20 to 30 cents per gallon).

THIN-FILM EVAPORATOR FIELD EVALUATION AT PLANT C

A 1-day site visit was conducted at Plant C in order to collect information on engineering design and cost, along with selected process samples (Allen, 1984c).

Process Description

Plant C uses thin film evaporation for the reclamation and recycle of organic solvents. The primary activity at Plant C is the reclamation of organic solvents and contaminated products for recycle or sale. Specialty solvent blends which are optimized for specific client uses are also produced. The solvent recovery processes include two VOC recovery systems: a Luwa thin-film evaporator and one SRS, Riston Batch Distillation.

Support facilities include a drum storage and management area, a cooling water system, an oil-fired boiler for steam generation, an air compressor, a bench-scale Rodney-Hunt thin-film evaporator, storage tanks, and associated pumps and piping.

The wastes processed by Plant C are from the chemical, plastics, paint, adhesive film, electronics, and photographic industries. The types of chemicals recovered included chlorinated solvents, freons, ketones, and aromatic hydrocarbons. There is currently no vacuum system and consequently no capability for operating the Luwa evaporator under reduced pressure. This precludes processing of high-boiling compounds such as naphtha and xylene.

Contaminated organic solvents are received at the plant in drums, and each drum is coded for identification in the drum storage area. A bench-scale distillation is normally done on each incoming shipment in order to determine recovery, efficiency, and materials characteristics. The standard recovery procedure is to process each batch of chemicals through the Luwa thin-film evaporator during which 70 to 95 percent of the material is stripped off as overhead product. However, nonflammable materials may be processed through an SRS 120 Riston evaporator instead of the Luwa when the capacity is needed.

This evaporator was designed for recovery of vapor degreasers (chlorinated solvents) and would not meet standards required for flammable materials.

The Luwa thin-film evaporator system consists of a 1.0 m^2 (10.8 ft^2) heat transfer surface Luwa evaporator, entrainment separator, condenser, product tank, feed recirculating tank, and pumps. Steam is used as the heating medium with the pressure being set typically between 207 kPa (30 psig) and 552 kPa (80 psig) depending upon the solvent being processed. The Luwa is operated at atmospheric pressure. The system process pumps are compressed air diaphragm pumps. A batch of solvent is charged to a 1,700-liter (450-gallon) feed recirculation tank. The overhead product from the evaporator is pumped into a 1,700-liter (450-gallon) product tank. The evaporator bottoms are pumped back to the feed tank, and the feed continues to recirculate until a predetermined VOC removal is reached. Process steam is generated in a 147 kW (15 hp) oil-fired boiler.

Process Effectiveness

Based on discussions with Plant C personnel and in the engineering judgment of the authors, the thin-film evaporator at Plant C can be used in the following treatment applications:

1. Removal of VOC from organic streams which may contain viscous high molecular weight organics or solids.

2. Removal of VOC from sludges such as insoluble organics and particulate solids.

3. Concentration of aqueous sludges such as insoluble organics and particulate sludges.

4. Removal of VOC from aqueous streams where the VOC volatility is higher than that of water.

5. Removal of water from streams containing relatively high concentrations of volatile organics of lower volatility than water (water removed as overhead product).

At the time of the visit, a batch of contaminated acetone was being processed through the Luwa evaporator (Figure 24). The reclaimed product was being stripped off overhead and pumped into a product receiver. The bottoms from the evaporator was being pumped back to the feed tank for recirculation through the Luwa. The condenser was vented to the outside of the building through a 1.25-cm (1/2-inch) pipe. Any emissions from this vent would normally be noncondensibles; but in the event of a condenser overload, it would be a source of VOC emission. The top of the feed tank and the top of the product tank consisted of movable lids which were not airtight, and this is a potential source of VOC emissions.

Grab samples were taken and the results of the analysis are reported in Tables 24, 25, and 26. The following samples were taken:

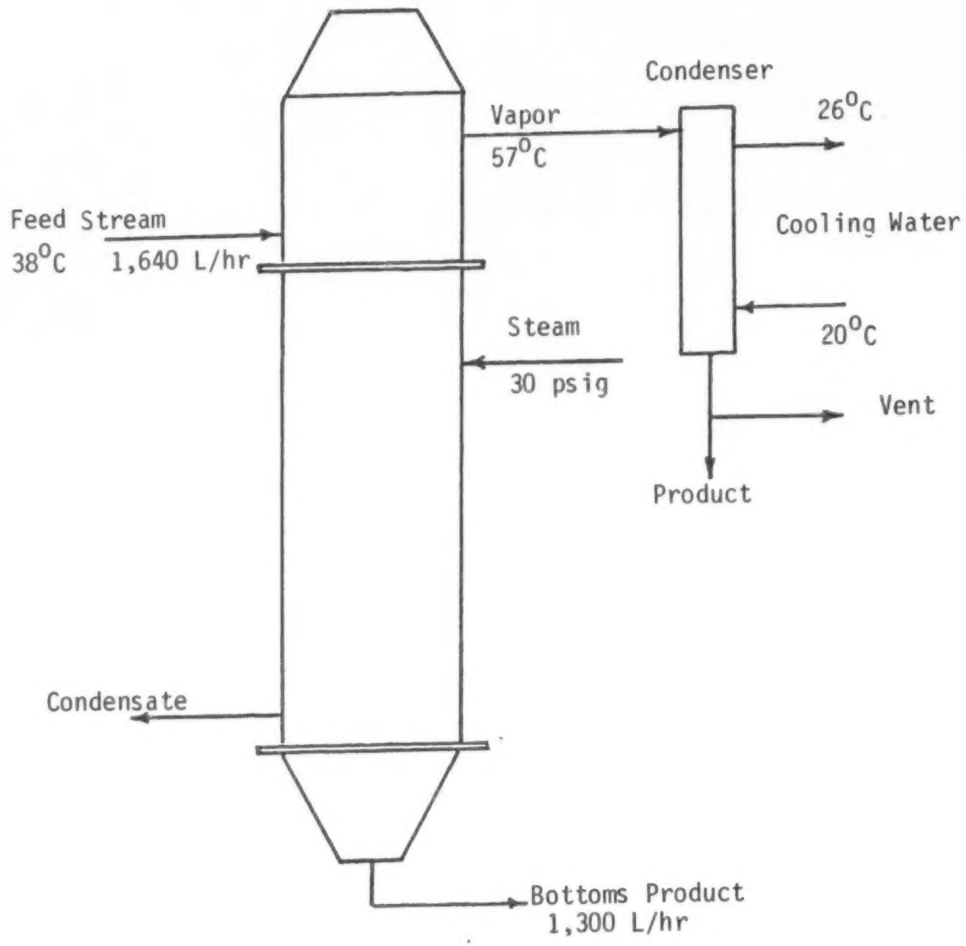

Condenser
Vapor
57°C
26°C
Cooling Water
Feed Stream
38°C
1,640 L/hr
Steam
30 psig
20°C
Vent
Product
Condensate
Bottoms Product
1,300 L/hr

Figure 24. Solvent recovery: Acetone.

TABLE 24. ANALYSIS OF LIQUID SAMPLES, THIN FILM EVAPORATOR, PLANT C

	Feed		Product		Bottoms	
	Liquid composition[a] (vol. %)	Headspace analysis (mg/L)	Liquid composition[a] (vol. %)	Headspace analysis (mg/L)	Liquid composition[a] (vol. %)	Headspace analysis (mg/L)
Acetone	74.3	378.0	82.2	383.0	60.6	308.0
Freon TF	0.1	2.0	<0.1	2.0	0.1	1.5
1,1,1-Trichloroethane	1.5	17.9	2.2	19.1	0.9	9.2
Trichloroethylene	0.2	0.1	0.3	0.1	<0.1	0.1
Toluene	0.5	0.3	0.9	0.2	0.9	4.1
Ethyl benzene	ND	0.1	0.3	<0.1	0.3	0.4
Xylene	5.9	2.1	2.0	0.2	<0.1	<0.1
Tetrachloroethylene	0.6	2.4	0.5	1.6	13.6	5.0

ND = not detected.

[a] Approximately 17 percent of the waste was high boiling organics and resins.

TABLE 25. ANALYSIS OF GAS SAMPLES FROM VENT OF THIN FILM EVAPORATOR, PLANT C

Compound	Concentration in Luwa vent (mg/L)
Acetone	0.04
1,1,1-Trichloroethane	0.003
Trichloroethylene	0.008
Tetrachloroethylene	0.003
Toluene	0.002
Ethyl benzene	0.002
Xylene	0.005

TABLE 26. ANALYSIS OF GAS SAMPLES FROM PRODUCT RECEIVER, PLANT C

	Air concentrations		Air emissions	
Compound	Test 1 (mg/L)	Test 2 (mg/L)	Test 1 (g/sec)	Test 2 (g/sec)
Acetone	5.3	7.2	0.565	0.70
Freon TF	0.04	0.04	0.004	0.004
1,1,1-Trichloroethane	0.41	0.45	0.043	0.043
Trichloroethylene	0.04	0.013	0.004	ND
Tetrachloroethylene	0.075	0.059	0.008	0.0057
Toluene	0.009	0.007	NS	NS
Ethyl benzene	0.016	0.007	NS	NS
Xylene	0.03	0.016	0.003	NS

NS = not significant concentrations above field blank.

Luwa feed stream,

Distillate,

Residue,

Condenser vent (gas), and

Product tank (gas).

In addition to the grab sample, the following process parameters were provided by Plant C during the field test:

1.	Feed rate	1635 L/hr (432 gal/hr)
2.	Feed temperature	38°C
3.	System pressure	760 torr
4.	Vapor temp.	57°C
5.	Steam pressure	310 kPa (30 psig)
6.	Jacket (upper) temperature	132°C
7.	Jacket (lower) temperature	107°C
8.	Condenser water inlet temperature	20°C
9.	Condenser water outlet temperature	25°C
10.	Distillate rate	344 L/hr (91 gal/hr)
11.	Bottoms rate (feed - distillate)	1291 L/hr (341 gal/hr)
12.	Luwa drive motor amps	1.1

The waste being processed in the Luwa evaporator was acetone containing xylene and low levels of chlorinated solvents. The acetone and other low-boiling point compounds were somewhat more concentrated in the distillate and xylene was enriched in the bottoms. Because of the requirements to maintain the resins in solution, the VOCs in the bottoms at the end of the run were not substantially different in concentration than the VOCs in the feed (although the volume of waste was reduced by about 70 percent).

Process Residuals

The analysis of the air samples from the process vent indicated that no significant (relative to the field blank) air emissions were observed from the process vent. The vent pipe was located perpendicular to the wind flow on the building exterior; and due to the wind gusts, air flowed alternatively in and out of the vent (as measured by the Alnor velometer). No odors were detected at the vent.

The product storage tank has a loose fitting steel top with a gap of approximately 8-3 cm (3-1 inch) and was 1 meter (4 ft) wide with an area of 620 cm^2 (0.67 ft^2). An MSA portable pump with 0.42 mL/count was used to draw air past a carbon adsorption bed. An Alnor Velometer Jr., Type 8100, was used to measure wind velocities. The wind was variable and five readings were taken during each air sampling procedure. The windspeed was 172 cm/sec (340 ft/min) on the first product storage test and 157 cm/sec (310 ft/min) on the second product storage test. The volumes of air sampled were 313 and 320 mL on tests 1 and 2 of the product storage tank. Acetone was the major component lost from the storage tank at 0.56 and 0.70 g/sec. Based on an emission factor of 2.5×10^{-5} g/mol/cm^2 sec obtained from the air emissions model of Thibodeaux and Parker (Spivey, 1984), a velocity of 170 cm/sec (340 ft/min), and a vapor concentration of 383 mg/L (measured at 25°C in the laboratory), the emissions for a fully exposed surface were estimated to be 2.0 g/sec, greater than the measured field rates by a factor of 3.

At the time of the test of the product storage tank, the plant was planning to replace the current receiver tanks with a more enclosed tank system.

Distillation residues which cannot be utilized as fuel in furnaces or cement kilns are being solidified with diatomaceous earth in drums for landfill disposal.

Process Cost

Equipment and operating costs were not readily available at the facility at the time of the visit. However, some information which may be relative to cost was provided.

- The Luwa evaporator was purchased rebuilt, and a condenser was fabricated to Luwa specifications. In retrospect, the owner would have purchased a package unit from Luwa because of factory assistance available with installation and startup operational problems.
- The 1.0 m^2 (10.8 ft^2) Luwa evaporator was reported to be rated at 378 liters/hr (100 gal/hr) distillate by Luwa. A high rate of 606 liters/hr (160 gal/hr) was achieved one time, with rates of 454 liters/hr (120 gal/hr) obtained frequently. Rates for chlorinated solvents which is the largest volume-type process, averages above 322 liters/hr (85 gal/hr).
- The plant is operated on a two-shift, 5-day work week. There are two production operators per shift.

Plant C provided limited process costs for the operation of the thin-film evaporator. Based on the information obtained from the batch being processed at the time of the site visit, Table 27 provides operating costs and an estimate of unit costs for waste treatment. The cost per unit of waste treated is greater than estimated for Plant A which used a larger unit.

TABLE 27. 1984 PLANT C OPERATING COSTS

Feed rate[a]	491 L/hr (130 gal/hr)
Overhead product, percent of feed[a]	70 percent
Labor[a]	$0.61/L ($2.31/gal. waste)
VOC recovery	344 L/hr (91 gal/hr)
Maintenance Materials	
Disposal by landfill	$0.24/L ($50/55 gal. drum) + labor and freight
Disposal by incineration	$0.21/L ($44/55 gal. drum) + labor and freight
Steam[a]	23 L/min
Cooling water[a]	110 L/min (30 gpm)
Annual system cost[a]	$125,000
ANNUAL COSTS	
Annual operating costs[b]	$150,400
Capital recovery factor (10 yr at 10 percent interest)	$20,343
Total	$171,000
UNIT COSTS	
$/L waste treated	0.048
$/L VOC recovered	0.057
$/Mg VOC recovered (density = .8 g/mL)	71

[a] Provided by Plant C.

[b] Assumed to equal 1 man/process x $24/hr x 24 hr/day x 300 days.

SECTION 8

FIELD TEST RESULTS: DIRECT STEAM STRIPPING

Plant D is a hazardous waste TSDF that uses steam stripping to recover VOCs from wastes. At Plant D, live steam is injected into a recycling waste material. The steam stripping unit used at Plant D was chosen for assessment because it can be commercially purchased and is suitable for treating wastes on the site of generation as well as offsite. The batch steam stripper can handle small batches of waste; wastes which vary in composition can be handled. Some reactive wastes can be processed in the unit more successfully than in a thin-film evaporator due to the lower processing temperatures. The wastes that are treated must be able to be pumped in the diaphragm recycle pumps: this imposes a limitation on viscosity and solids. When the VOC of interest is of low volatility and high waste solubility, the concentration in the condensed steam may be lower than in the initial waste. The direct steam stripper would not be able to recover the VOC in such a system. When the VOCs separate as an organic layer in the condensed steam, direct steam stripping can be used for recovery. The direct steam stripping process can be used for organic and aqueous batches of waste contaminated with solids, sludges, oils, and grease.

PROCESS DESCRIPTION

Plant D is engaged in the reclamation of organic solvents for recycle and sale. A live steam stripping process is used for organic solvent reclamation. The steam stripping system is a package unit manufactured by and purchased from DCI, Inc. (DCI, Inc., 5725 W. 79th Street, Indianapolis, IN 46268). This system is located inside a building which also contains three 3,800-liter (1,000-gallon) waste solvent storage tanks and three 3,800-liter (1,000-gallon) product storage tanks. The building is also utilized for drum storage. There are five 38,000-liter (10,000-gallon) outside storage tanks which are used primarily for contaminated solvent and residue storage. An oil/gas-fired boiler system is used for process steam generation. An analytical laboratory is maintained in the building housing company offices.

The contaminated organics processed by Plant D are generated mostly by the chemical, paint, pharmaceutical, plastics, and heavy manufacturing industries. The types of chemicals recovered include the following VOCs: ketones, aromatic hydrocarbons, chlorinated solvents, freons, and petroleum naphthas. The recovered products may be recycled back to the generator or marketed to suitable end users. Generally, 50 to 70 percent solvent recovery from the waste stream is expected. Residues from the stripping process are solidified by mixing with sorbents and shipped offsite to be landfilled.

The steam stripping system (a schematic is shown in Figure 25) consists of a stripping vessel, overhead vapor condenser, distillate receiver,

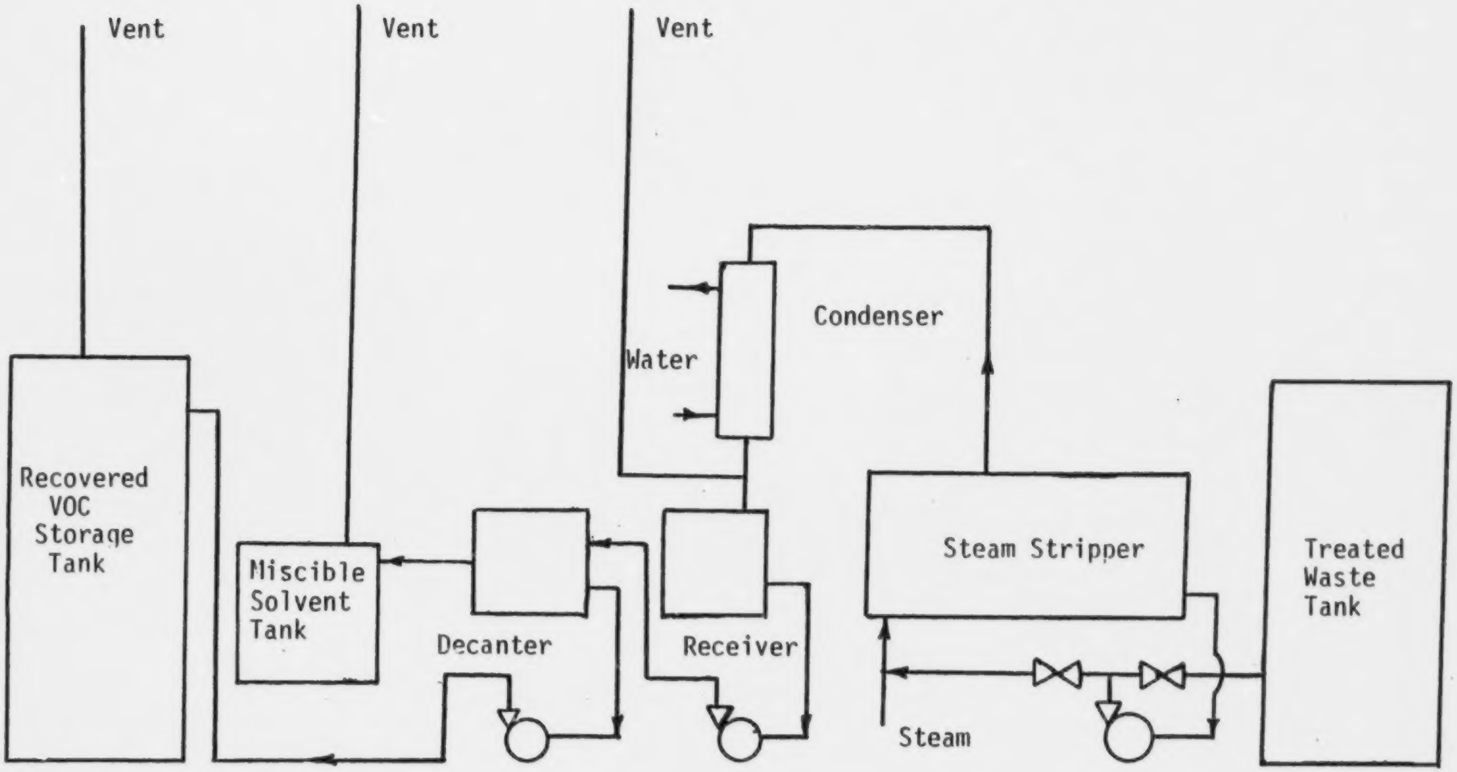

Vent
Vent
Vent
Water
Condenser
Recovered VOC Storage Tank
Miscible Solvent Tank
Decanter
Receiver
Steam Stripper
Steam
Treated Waste Tank

Figure 25. Batch steam stripping process.

decanter, miscible solvent tank, product storage tanks, a residue tank and associated pumps and support facilities.

The steam stripper is a 1,900-liter (500-gallon) stainless steel horizontal tank containing a steam sparger running lengthwise along the bottom. A recirculating pump discharging into the steam sparger promotes steam and solvent contact. Steam pressure to the sparger is normally controlled at 150 kPa (20 psig).

The overhead product condenser is a vertical, shell-and-tube, water-cooled condenser which discharges into a distillate receiver. The distillate receiver is vented through a pipe extending through the roof. The distillate is pumped from the receiver to a decanter from which the aqueous phase flows by gravity to a miscible solvent tank, with the organic phase being pumped to a product storage tank.

The process steam is supplied by an oil/gas boiler rated at 3,900 kW (400 HP) and 1,000 kPa (150 psig). The boiler is currently being operated on gas, utilizing about 500 kW (60 HP), and producing steam at 690 kPa (100 psig).

The distillate condenser/receiver is vented to the atmosphere where emissions were expected to be mostly noncondensibles. However, this is a potential source of volatile organic compound (VOC) emissions should the condenser become overloaded for any reason. Emissions from storage tank vents would represent operational displacement of equilibrium vapor from the tank headspace.

The steam stripper is primarily utilized for solvent reclamation, although some incidental aqueous stream treatment results. On occasion, the system has also been utilized for treatment of dilute aqueous streams solely to reduce the organic content to a level that is acceptable to the local municipal waste water treatment facility.

The typical operation involves charging a 950-liter (250-gallon) batch of organic solvent to the stripper, steam stripping the solvent overhead, and decanting the distillate when the solvent is immiscible with water, which is the case with most of the solvents processed. A typical batch of 950 liters (250 gallons) can be processed in one hour. The aqueous phase from the decanter is collected in a 1,100-liter (300-gallon) miscible solvent tank (MST). The contents of the MST are ultimately processed again through the stripper for recovery of residual solvent. In many cases, the aqueous residual in the stripper after the MST contents have been processed is suitable for discharge to municipal waste water treatment systems. The volume of organic residues left in the stripper is approximately 260 liters (70 gallons). They are typically burned in an incinerator or solidified and landfilled. Aqueous residues from the stripper (which contain soluble organics) are not suitable for use as fuel, since steam condensate reduces the heat value to an unsatisfactory level. This residue is currently being solidified and landfilled.

Processing of solvents which are miscible in water may involve multiple strippings, giving the effect of fractionation, depending upon the degree of dryness required. The concentration of the solvents in the condensate must be greater than in the batch for this to occur.

PROCESS EFFECTIVENESS

Plant D stripped waste material by direct injection of live steam into a waste batch. The process of stripping continued until the desired concentrations were achieved in the waste. Four batches of waste were evaluated: (1) an aqueous xylene batch, (2) a chlorinated organic-oil mixture, (3) a chlorinated organic-water mixture (1,1,1-trichloroethane), and (4) a mixture of solvents and water. A summary of the waste characterization and process data is presented in Table 28. The individual components in the waste are presented in Tables 29, 30, 31, and 32.

The results of analyzing waste material during stripping is presented in Tables 33, 34, 35, and 36. Only the major compounds detected in the analyses are reported in these tables; compounds below the detection limit are reported in the field test report (Allen, 1985d). These results are also presented in log normal plots in Figures 26, 27, 28, and 29. In general, each of the curves for the VOC removal by the process was linear; an exponential first order decay was indicated for each major volatile component. Further time in the stripper would reduce the VOC concentration. The second batch was an exception; the concentration of trichloroethane in the second batch did not initially decay at the exponential rate because the other component (methyl ethyl ketone) boiled off first.

The aqueous xylene batch (Batch 1) contained organic and water phases and a small amount of solids (Table 26). The organic phase constituted approximately 25 percent of the waste volume and was composed predominantly of xylene. The aqueous xylene batch initially contained 1,260 L and the final batch size was 1,420 L. Recovery of 333 L of organic distillate was achieved, with 248 L of aqueous distillate going to the MST. The steam rate was 250-270 kg/hr and the heatup and stripping time was 2.08 hr. The removal rates of all the compounds appeared to be approximately the same, with the heavier materials being somewhat more slowly removed (Table 33, Figure 26). A detailed evaluation is found later in this section. There was removal of all the VOCs to less than 300 ppm in the final treated waste.

In the 1,1,1-trichloroethane batch (Batch 2), two major components were removed from the organic waste. These were trichloroethane and methyl ethyl ketone. The 1,1,1-trichloroethane batch initially contained 897 L of VOC in oil. The final batch volume was 320 L of oil and water. Recovery of 670 L of VOCs was achieved as organics, and 400 L of aqueous distillate were generated. The steam flow rate was 250-300 kg/hr and the heatup and stripping time was 1.72 hr. Methyl ethyl ketone was quickly removed from the process with only 23 ppm remaining after 80 minutes (Table 34, Figure 27). The trichloroethane was somewhat more slowly removed with 4,000 ppm or 0.4 percent residual trichloroethane in the oil material at the end of the batch. Since the methyl ethyl ketone boiled off first, the concentration of the trichloroethane did not drop initially but appeared to decrease much more rapidly in the later stripping as the batch temperatures increased.

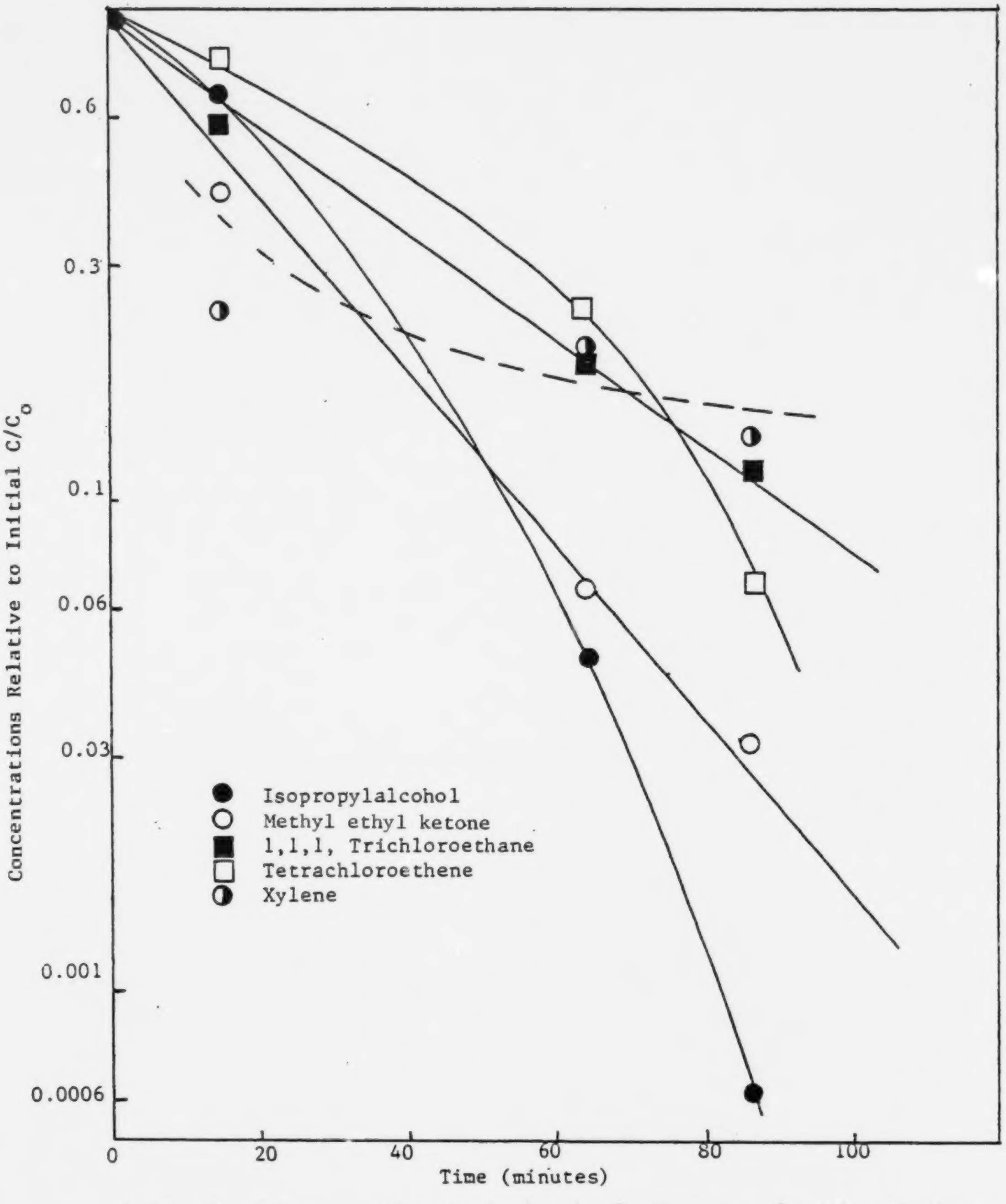


Figure 26. Concentrations in the batch of waste as a function of time: xylene MST.

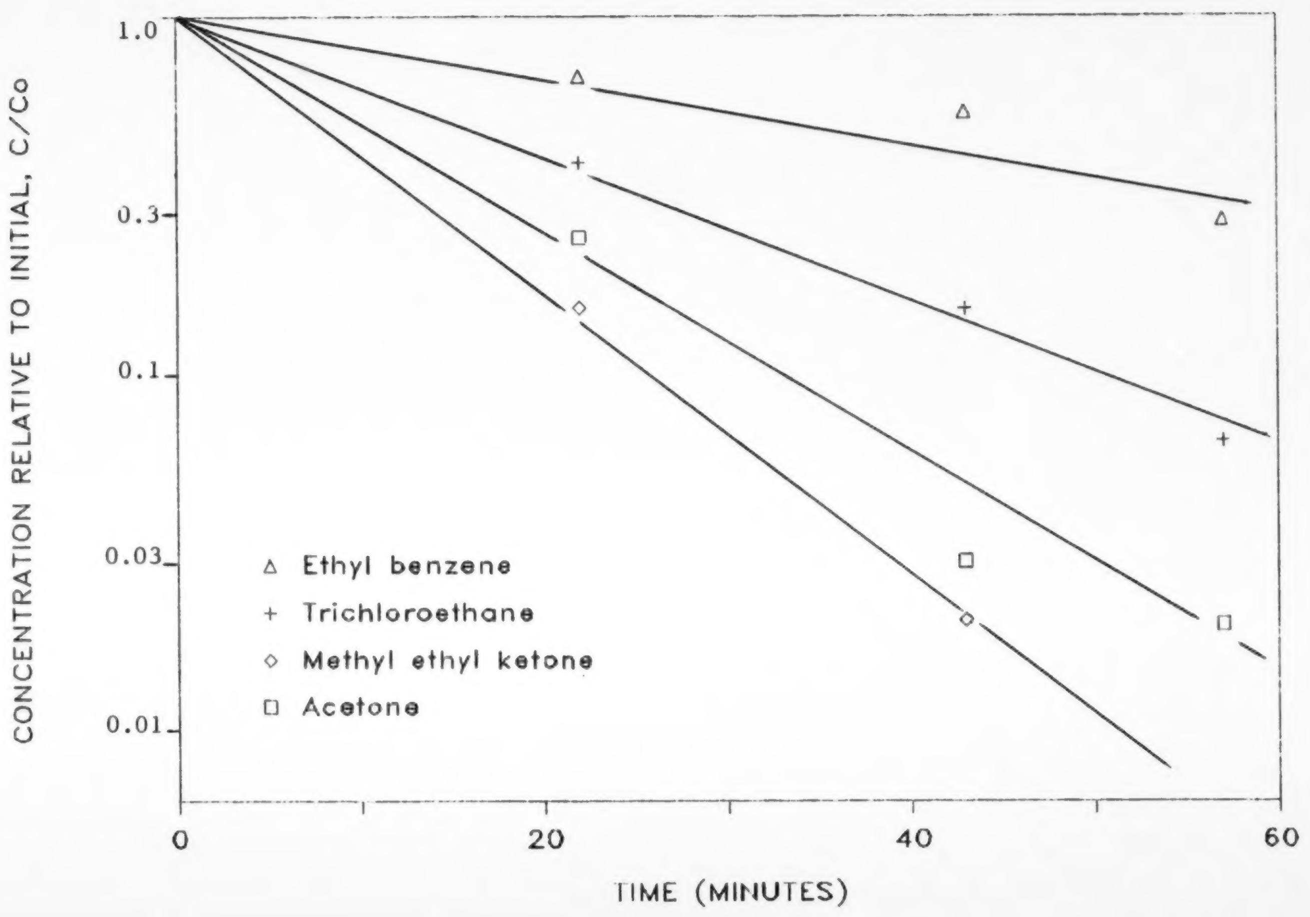


Figure 27. Concentrations in the batch of waste as a function of time: trichloroethane MST.

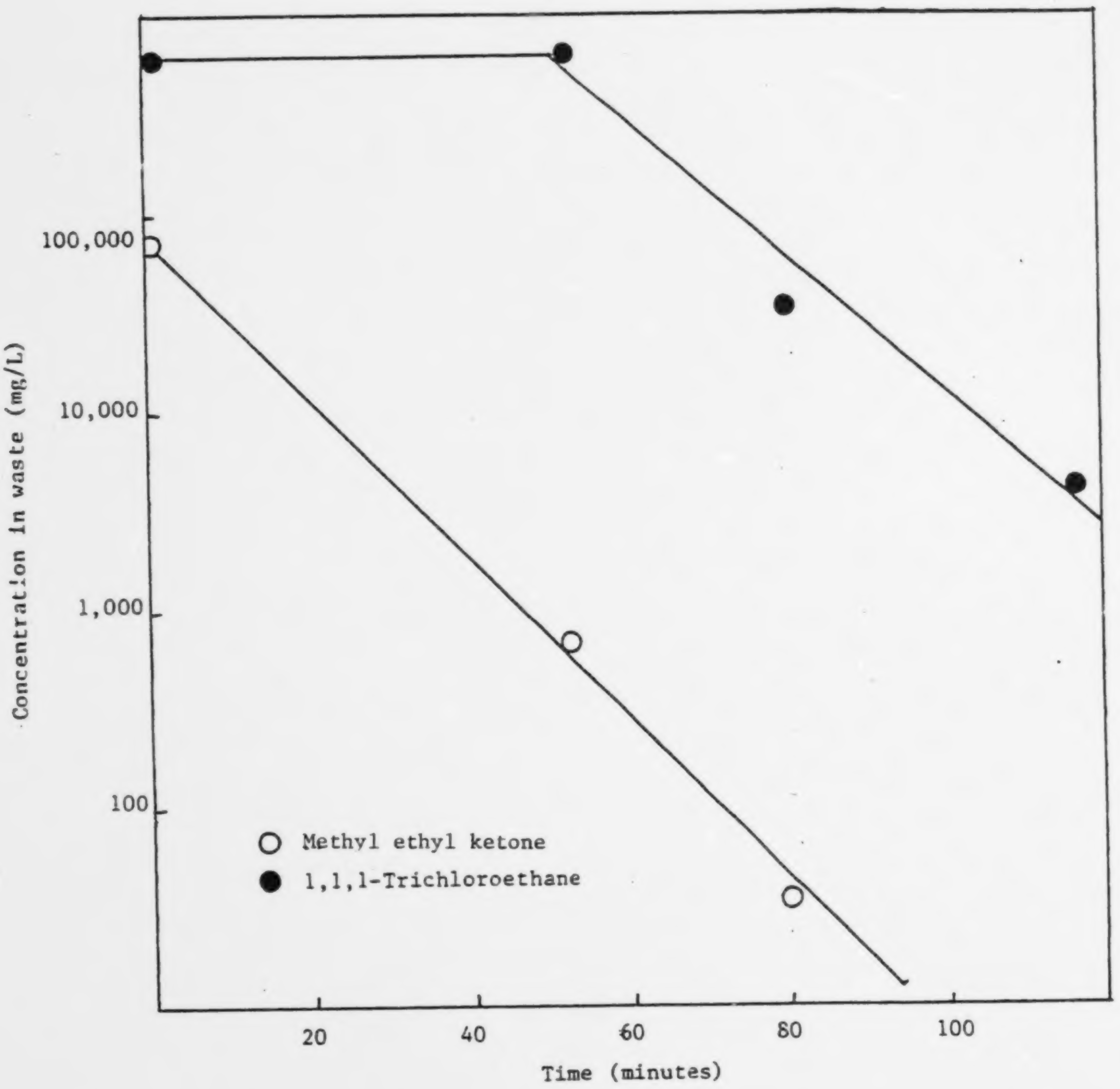


Figure 28. Concentrations in the batch of waste as a function of time: 1,1,1 trichloroethane.

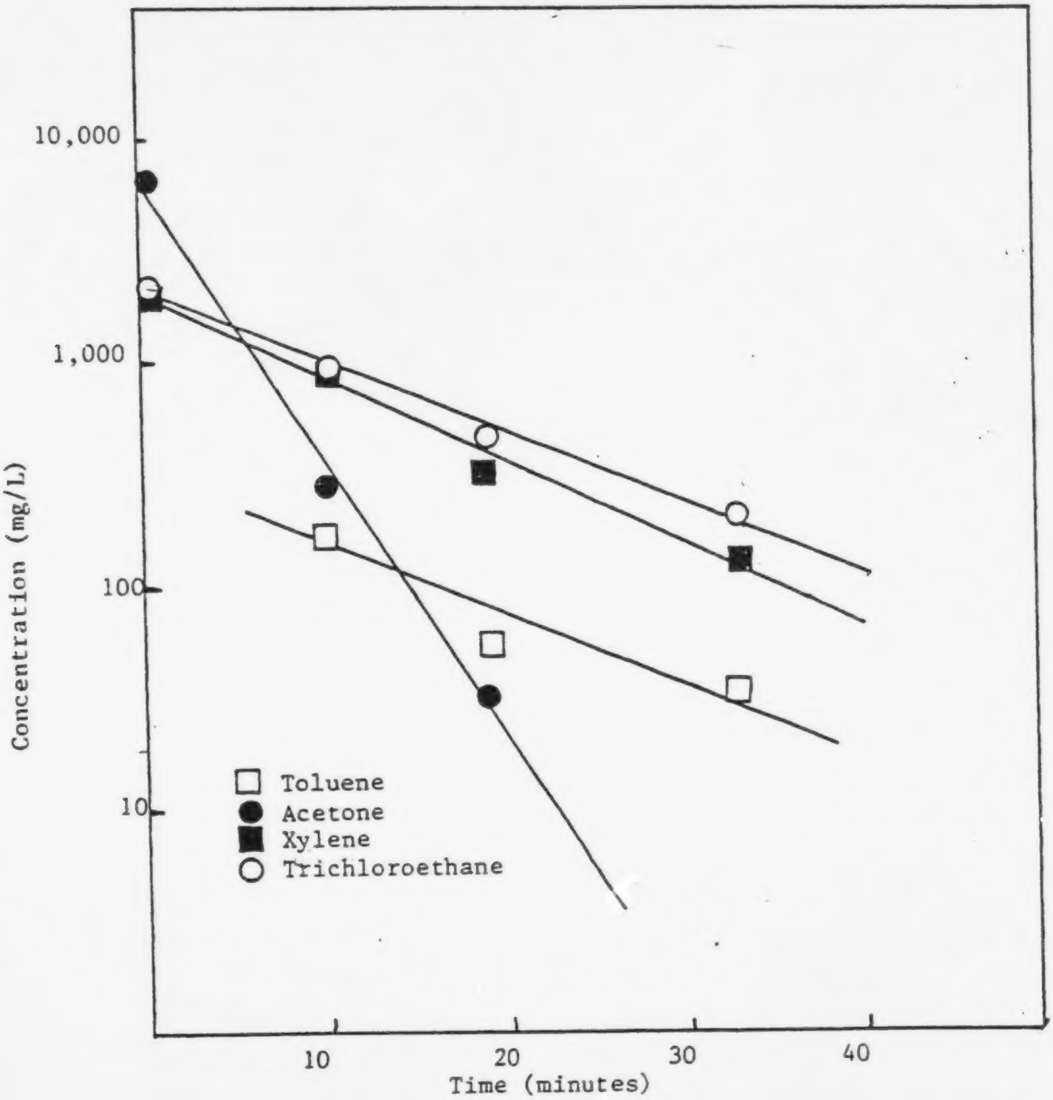


Figure 29. Concentrations in the batch of waste as a function of time: Mixed solvent batch.

TABLE 28. WASTE CHARACTERIZATION AND PROCESS DATA

	Batch 1	Batch 2	Batch 3	Batch 4
WASTE CHARACTERISTICS				
Initial volume (L)[a]	1,260[b]	897	564	360
VOC content (mass percent)[a]	18.7[c]	74[d]	18	3.1[e]
Water content (L)[a]	1,253	f	460	357
Oil content (L)[c]	f	233	f	f
PROCESS DATA				
Stripping time (min)[a]	86	87	57	33
Steam rate (L/min)[g]	4.3	4.5	4.5	4.0
VOC stripping rate[a] constant (min^{-1})	0.073	0.060	0.048	0.132
Bottoms VOC content (wt. percent)[a]	0.05	0.41[d]	1.2	0.04
VOC recovered (L)[a]	333	670	45	3.2
Stripper residue volume (L)[a]	1,420	320	545	349
Stripper oil content (L)[c]	f	233	f	f
Stripper water content (L)[a]	1,420	87	539	344
Condensed steam (L)[a]	248	400	180	140
Percent VOC removed[a]	99.8	99.8	93	99

[a] Measured.

[b] Volume charged to stripper. See Table B-3.

[c] Not measured, estimated by material balance, density = 0.866 (refer to sample calculations in Appendix F).

[d] Volume percent, measured.

[e] Second phase measured by volume as added to water.

[f] Negligible.

[g] Not measured, estimated by enthalpy balance.

TABLE 29. WASTE CHARACTERIZATION OF BATCH 1 (AQUEOUS XYLENE)

Number of Phases	2
Total solids (mg/L)[a]	880
Water (weight percent)	81.3
Oil (weight percent)	Negligible
VOC (weight percent)[b]	18.7
Aqueous Phase	
pH	6.1
Density	1.0
VOC Analysis:	(mg/L)
Acetone	39
Isopropanol	960
Methyl ethyl ketone	1,040
1,1,1-trichloroethane	170
Tetrachloroethene	290
Ethyl benzene	360
Toluene	86
Xylene	2000
Organic Phase	
Density (g/cm^3)[c]	0.866
Composition:	
Xylene	×70%
Other aromatics	×30%

[a] The solids were in the aqueous phase.

[b] Most of the VOC was apparently in the organic phase.

[c] Based on density of toluene, not measured.

TABLE 30. WASTE CHARACTERIZATION OF BATCH 2
(1,1,1-Trichloroethane/Oil)

Number of Phases	1
Total Solids (mg/L)	2,800
pH	4.0
Water (volume percent)	-
Oil (volume percent)	26
VOC (volume percent)	74
Methyl ethyl ketone (volume percent)	7.5
1,1,1-Trichloroethane (volume percent)	66.0
Density (g/mL)	1.2[a]

[a] Estimated from pure components.

TABLE 31. WASTE CHARACTERIZATION OF BATCH 3
(1,1,1-Trichloroethane/Water)

Number of Phases	2
Total Solids (mg/L)	130
pH	5.8
Water (weight percent)	82
Oil (weight percent)	-
VOC (weight percent)	18
Density (g/mL)	1.0[a]
VOC Analysis (Aqueous Phase)	
Methyl ethyl ketone (mg/L)	320
1,1,1-Trichloroethane (mg/L)	180,000
Ethyl benzene (mg/L)	44
Acetone (mg/L)	290
Isopropanol (mg/L)	37

[a] Estimated as the density of water.

TABLE 32. WASTE CHARACTERIZATION OF BATCH 4
(Mixed Solvent/Water)

Number of Phases	2
Description of Secondary Phase	Xylene, toluene
Total Solids (mg/L)	130
pH	7.0
Water (weight percent)	97
Oil (weight percent)	-
VOC (weight percent)[a]	3.1
Density (g/cm^3)	1.0
VOC Analysis (Aqueous Phase)	
Acetone (mg/L)	6,500
Isopropanol (mg/L)	95
Methyl ethyl ketone (mg/L)	112
1,1,1-Trichloroethane (mg/L)	2,200
Tetrachloroethene (mg/L)	55
Toluene (mg/L)	86[b]
Xylene (mg/L)	4[b]

[a] Measured volumetrically as added to batch initially.

[b] The low values are thought to be due to incomplete initial mixing in the stripping vessel. Values were not used in stripping rate analysis. The recovered VOCs were measured, and VOCs were added to the batch.

TABLE 33. WASTE VOC CONCENTRATION DURING STRIPPING: BATCH 1 (AQUEOUS XYLENE)

Process time (min)	Sample number	Concentration (mg/L)							
		Acetone	IPA	MEK	TCEA	TCE	EB	Toluene	Xylene
0	45-3	39	960	1,040	170	290	360	86	2,000
15	45-5	10	640	460	99	230	560	32	480
64	45-6	<6	47	70	33	72	56	17	410
86	45-7	<6	<6	34	20	<20	100	42	270

IPA = isopropanol
TCE = tetrachloroethene
MEK = methyl ethyl ketone
EB = ethyl benzene
TCEA = 1,1,1-trichloroethane

TABLE 34. WASTE VOC CONCENTRATIONS DURING STRIPPING: BATCH 2 (1,1,1-TRICHLOROETHANE/OIL)

Process time (minutes)	Sample number	Concentration (mg/L)	
		1,1,1-trichloroethane	Methyl ethyl ketone
0	45-22	660,000	75,000
28	45-24	690,000[a]	591[a]
55	45-25	22,000[a]	<7[a]
87	45-26	4,100	<7

[a] Sample 45-24 was unsuitable for direct liquid analysis: the vapor concentrations could be measured, however, and the liquid concentrations were estimated by using Henry's constant calculated from the data obtained from the analysis of sample 45-22. The same procedure was used for comparision purposes with sample 45-25, and values of 8,70 mg/L and 23 mg/L were obtained for 1,1,1-trichloroethene and methyl ethyl ketone. When compared with 22,000 mg/L and <7 mg/L, respectively, it appears that the estimates for Sample No. 45-23 are probably good to within a factor of 5.

TABLE 35. WASTE VOC CONCENTRATIONS DURING STRIPPING: BATCH 3 (1,1,1-TRICHLOROETHANE/WATER)

Process time (minutes)	Sample number	Concentration (mg/L)				
		Acetone	MEK	TCEA	Ethyl benzene	IPA
0	45-29	290	320	180,000	44	37
22	45-31	71	50	71,000	30	<6
43	45-32	9	<7	28,000	24	<6
57	45-33	<6	<7	12,000	12	<6

MEK = methyl ethyl ketone
TCEA = 1,1,1-trichloroethane
IPA = isopropanol

TABLE 36. WASTE VOC CONCENTRATIONS DURING STRIPPING: BATCH 4 (MIXED SOLVENT/WATER)

Process time (minutes)	Sample number	Concentration (mg/L)			
		Acetone	Toluene	Xylene	TCEA
0	45-11	6,500	86[a]	4[a]	2,200
10	45-15	270	170	900	930
19	45-16	32	56	310	460
33	45-17	<6	35	120	230

[a] The low values are thought to be due to incomplete initial mixing in the stripping vessel. Values were not used in stripping rate analysis. The VOCs were added to the batch, and the recovered VOCs were measured.

TCEA = 1,1,1-trichloroethane

When the batch of waste trichloroethane (Batch 2) had been processed, a residual tank of condensed steam containing some of the volatile organics was added to other miscible solvent residuals in the miscible solvent tank to constitute the third batch tested. The resultant mixture was a two-phase chlorinated organic-water batch. The organic phase constituted approximately 18 percent of the volume of the batch. Batch 3 initially contained 564 L and was stripped to 545 L of residuals. Recovery of 45 liters of organics was achieved, with an aqueous distillate volume of 180 L. The steam rate was 270 kg/hr and the heatup and stripping time was 0.95 hr. As this aqueous waste was stripped, the concentrations of the volatile materials were measured (Table 35, Figure 28). In this batch of aqueous waste (which differed from the aqueous xylene batch in that there was no organic phase of xylene present during stripping), the stripping rates varied for the different compounds, with the more volatile materials such as chloroform and acetone stripped at a relatively faster rate. As seen from Figure 28, an approximately logarithmic decrease in the concentrations of the major volatiles was observed. The major component present in the aqueous waste was trichloroethane, and the waste was stripped down to 1 percent trichloroethane in 60 minutes. It is estimated that another 40 minutes stripping would be required to drop the trichloroethane level to 0.1 percent based on the extrapolated curve in Figure 30.

The fourth batch tested was an aqueous mixed solvent batch. The batch had an aqueous phase of predominantly acetone, trichloroethane, xylene, and toluene which constituted approximately 3 percent of the waste by volume. The initial batch charge was 360 L. Recovery of 3.2 liters of immiscible VOCs was achieved, together with 140 L of condensed steam. The steam rate was 230-250 kg/hr and the heating and stripping time was 0.83 hr. The effectiveness of the process for removal of VOCs from the mixed solvent batch is presented in Table 36 and Figure 29. The concentrations of each of the volatile components were reduced to less than 0.03 percent after 33 minutes of stripping. The toluene, xylene, and trichloroethane stripped at approximately the same rate, with acetone approximately twice as fast. Laboratory analyses of the charge samples indicated that the initial concentrations of toluene and xylene were not the same as initially charged to the batch (approximately 4 L of toluene and xylene mixture was charged to the batch), apparently because of inadequate mixing in the batch while the sample was taken.

As the waste material is stripped, the headspace equilibrium concentration of the volatile organic compounds in the cooled waste decreases. In Tables 37, 38, 39, and 40, it is apparent that the volatility characteristics of the wastes are dramatically altered by the steam stripping process. These volatility characteristics of the cooled wastes are of concern because of the relation between the vapor pressures of the volatile components and their release into the atmosphere upon disposal. The waste material generally showed at least an order of magnitude decrease in the vapor concentrations at equilibrium with the waste.

Table 41 presents a summary of the data analysis of the liquid phase compositions for the four batches evaluated at Plant D. Linear correlations of the logarithm of the waste component compositions with the stripping time were performed. The correlation coefficient was relatively high for many of

TABLE 37. HEADSPACE CONCENTRATIONS[a] OF VOC AS A FUNCTION OF THE STRIPPING TIME: BATCH 1 (Aqueous Xylene)

Process time (minutes)	Sample number	Concentrations (mg/L)							
		Isopropanol	Acetone	MEK	TCE	TCEA	Toluene	Xylene	EB
0	45-3	0.53	0.11	5.2	1.3	3.9	8.1	16	4.6
15	45-5	0.16	<0.1	7.4	0.66	0.24	5.6	17	4.6
64	45-6	<0.1	<0.1	0.13	<0.1	<0.1	0.12	2.4	0.53
86	45-7	<0.1	<0.1	0.97	<0.1	<0.1	0.42	1.8	0.59

TCEA = 1,1,1-trichloroethane
MEK = methyl ethyl ketone
EB = ethyl benzene
TCE = tetrachloroethene

[a] Waste sample at 25°C.

TABLE 38. HEADSPACE CONCENTRATIONS OF VOC[a] AS A FUNCTION OF THE STRIPPING TIME

Batch 2 (1,1,1-Trichloroethane/Oil)

Process time (minutes)	Sample number	Vapor concentrations (mg/L)	
		Methyl ethyl ketone	1,1,1-Trichloroethane
0	45-22	104	440
28	45-24	0.82	460
55	45-25	0.032	5.8
87	45-26	0.02	0.91

[a] Waste sample at 25°C.

TABLE 39. HEADSPACE CONCENTRATION[a] OF VOC AS A FUNCTION OF THE STRIPPING TIME: BATCH 3 (1,1,1-Trichloroethane/Water)

Process time (minutes)	Sample number	Vapor concentrations (mg/L)				
		Methyl ethyl ketone	Acetone	1,1,1- trichloroethane	Ethyl benzene	Trichloroethylene[b]
0	45-29	11	0.22	440	0.24	0.3
22	45-31	0.2	<0.1	24	0.34	0.13
43	45-32	<0.02	<0.1	4.7	0.29	<0.1
57	45-33	<0.02	<0.1	2.1	<0.1	<0.1

[a] Waste sample at 25°C.

[b] Not detected in liquid above limit of detection.

TABLE 40. HEADSPACE CONCENTRATION[a] OF VOC AS A FUNCTION OF THE STRIPPING TIME: BATCH 4 (Mixed Solvent/Water)

Process time (minutes)	Sample number	Concentration (mg/L)				
		Methylene chloride[b]	Acetone	1,1,1-Trichloroethane	Toluene	Xylene
0	45-11	0.65	8.5	19	7.6	15
10	45-15	<0.1	0.33	<0.1	0.47	2.8
19	45-16	<0.1	0.17	0.9	0.14	1
33	45-17	<0.1	<0.1	1.7	<0.1	0.58

[a] Waste sample at 25°C.

[b] Methylene chloride was present below the detectability limit in the liquid phase (Table 30).

TABLE 41. LINEAR CORRELATION OF THE LOGARITHM OF THE WASTE CONCENTRATION WITH THE STRIPPING TIME

Batch	Component	Correlation coefficient	Stripping rate constants	
			(min^{-1})	(dimensionless)[a]
1	Acetone	-0.817	0.0246	7.14
1	Isopropyl alcohol	-0.988	0.0581	16.9
1	Methyl ethyl ketone	-0.998	0.0393	11.4
1	1,1,1-Trichloroethane	-0.9971	0.0242	7.0
1	Tetrachloroethane	-0.975	0.0296	6.47
1	Ethyl benzene	-0.85[b]	0.023	6.58
1	Toluene	-0.52[b]	0.0088	2.54
1	Xylene	-0.84[b]	0.0180	5.22
2	Methyl ethyl ketone	-0.999	0.1763	34.8
2	1,1,1-Trichloroethane	-0.944	0.0648	12.7
3	Acetone	-0.993	0.0806	10.0
3	Methyl ethyl ketone	-1.0[c]	0.0844	10.5
3	1,1,1-Trichloroethane	-0.9971	0.0468	5.82
3	Ethyl benzene	-0.950	0.021	2.59
4	Acetone	-0.997	0.280	25.4
4	Toluene	0.908[d]	0.127	5.97
4	Xylene	0.977[d]	0.110	7.8
4	1,1,1-Trichloroethane	-0.990	0.0684	6.21

[a] The dimensionless rate is obtained by dividing the rate constant (min^{-1}) by the ratio of the steam rate (L/min) to the amount of waste (L).

[b] The lower correlation coefficients could be due to the presence of an aromatic layer in the batch.

[c] The values of concentration below the detection limit were not used in these calculations; only two concentrations were available for the calculation.

[d] The estimated concentration at zero time was used in the correlation: the vapor pressure was measured and Henry's constant was calculated from the second sample set.

the rates of stripping. The steam rate influences the rate of stripping, so the rate constants are presented in a dimensionless form to account for the steam rate and batch size. Theoretically, the dimensionless rate is numerically equal to Henry's constant for equilibrium partitioning.

The mass flow rate of gas leaving the stripper is approximately equal to the steam rate, particularly for low concentrations of VOCs in waste water. The ratio of the mole fraction of a compound in the vapor phase to the mole fraction in the liquid phase is the equilibrium partition constant, K, in units of atmospheres per mole fraction. Defining [Ca] as the instantaneous concentration of a compound, the stripping rate constant ($\min^{-1}$) for the removal of VOC from the batch equals the steam rate, S (moles/sec), times K (moles of compound/mole steam/moles of compound in batch x moles water in batch), divided by the batch size B (moles water in the batch).

$$\frac{1}{[Ca]} \frac{d[Ca]}{dt} = - \frac{SK}{B}$$

The dimensionless rate constant is obtained by multiplying the stripping rate constant by the ratio of the batch size B to the steam rate. For equilibrium controlled processes, the dimensionless rate constant equals the equilibrium partition coefficient.

Henry's constants as reported in the literature for the laboratory measurement conditions are substantially greater for organics in aqueous streams than was measured in the laboratory for the wastes treated. The Henry's constants calculated from the headspace analysis and the liquid analysis (Appendix A) are compatible with the observed low values of the dimensionless rate constants. The use of Henry's constants given in the literature to predict stripping rates would seriously underestimate the times and costs that were observed in the field.

Although the partition coefficients estimated from the stripping data are much lower than literature values, the coefficients are similar for the same components in the various wastes. For example, the value of the partition coefficient of MEK was 11.4 and 10.5 in the aqueous batches. In the organic waste, the value of the partition coefficient was 34.8. In the aqueous wastes, the partition coefficient of 1,1,1-trichloroethane was 7.0, 5.82, and 6.21 for Batches 1, 3, and 4, respectively. To estimate the effectiveness of steam stripping to remove VOCs, it is desirable to measure the partition coefficient either by headspace methods or by process evaluation.

PROCESS RESIDUALS

Air Emissions

The air emissions were estimated for two batches, the xylene aqueous batch (Batch 1) and the production waste trichloroethane batch (Batch 2). The results of the concentrations obtained from air samples taken from the condenser vents are presented in Tables 42 and 43. In addition to the concentrations in the air samples, some of the equilibrium vapor analyses obtained on liquid samples are presented in Tables 42 and 43 for comparison.

TABLE 42. GAS PHASE VOC CONCENTRATIONS: BATCH 1 (AQUEOUS XYLENE)

Process time (minutes)	Sample number		Concentration (mg/L)						
			MEK	IPA	TCEA	TCE	Toluene	Xylene	EB
NA	46-1	Trip blank	<0.1	<0.1	<0.1	<0.1	<0.1	0.3	0.14
59	46-3	Condenser vent	8.8	2.2	2.1	1.1	6.4	2.3	1.2
63	46-2	Condenser vent	7.6	1.8	1.7	.97	7.0	4.3	1.7
65	46-5	Condenser vent	6.8	1.7	1.5	.87	6.6	3.7	1.6
74	45-10	Distillate headspace[a]	26	5.5	2.2	1.3	11	17	5.2
NA	45-9	Organic composite distillate headspace[b]	11	25	2.5	2	13	16	5.1
NA	45-8	Aqueous composite distillate headspace[c]	11.2	1.8	0.43	<0.1	0.16	0.36	0.65

MEK - methyl ethyl ketone
IPA - isopropanol
NA - not applicable
TCE - tetrachloroethylene
TCEA - 1,1,1-trichloroethane
EB - ethyl benzene

[a] Collected from the receiver
[b] Collected from the organic product storage tank
[c] Collected from the miscible solvents tank

TABLE 43. GAS PHASE VOC CONCENTRATION: BATCH 2
(1,1,1-Trichloroethane/Water)

Process time (minutes)	Sample number		Concentration (mg/L)				
			Methylene chloride	MEK	TCEA	Toluene	Xylene
-2[a]	49-2	Condenser vent	3.0	104	210	0.13	0.17
46[b]	49-3	Condenser vent	<0.1	0.34	22	0.10	0.61
47[b]	49-4	Condenser vent	0.12	2.4	85	0.18	0.63
43	49-5	Product storage vent	0.2	0.22	4.5	1.3	1.8
44	45-27	Product storage tank (lab headspace)	0.28	5	460	0.18	0.74
42	49-1	MST tank vent	<0.1	0.64	24	0.62	1.4
125	45-28	MST Tank (lab headspace)	0.88	74	560	<0.1	<0.1

[a] During batch heating, 2 minutes before stripping started.

[b] Midcycle sample.

MEK = methyl ethyl ketone

TCEA = 1,1,1-trichloroethane

The results of air emission measurements for Batch 1 are presented in Table 42. The concentrations of the equilibrium vapor over the distillate obtained midway through the process corresponded with the gas concentrations obtained in the vent during the process. The correspondence of the air emission concentrations in the vent with the headspace concentrations of the distillate (obtained at approximately the same time) was better than for either the product storage equilibrium concentrations or the aqueous composite distillate concentrations.

The average emissions are expected to be a function of both the rate of flow and the composition drift of the various components. Table 44 estimates the air emissions on the basis of the average of the results of the tests on the three air samples taken from the aqueous xylene batch; it was assumed that the VOC concentration in the air was constant throughout the batch operation. The volume emitted from the condenser vent was estimated on the basis of the data obtained from the integrated flow as determined by dry gas meter readings (Allen, 1985d). In Batch 1 (aqueous xylene) the dry gas meter recorded a 683-liter (24.2 cubic foot) flow over a time of 108 minutes. Since the process time (filling to stop stripping) was 125 minutes, the estimated total volume during the process was 790 liters. The emission factors were estimated by obtaining the ratio of the estimated grams of emissions to the total amount of wastes charged into the system and the total amount of volatile materials recovered. Emission rates are calculated by obtaining the ratio of the grams emitted to the process time (sec). The data that were used in the calculations are presented in Table 44. The emission rate was 0.0029 mg/sec for (aqueous xylene) Batch 1. This value should only be used in health effect calculations with care since the rates would not necessarily apply to processing other wastes and does not reflect process downtime. The emission factors in terms of g/g waste are expected to be more appropriate for dispersion modeling calculations.

In Table 43, the air emission results from the 1,1,1-trichloroethane batch (Batch 2) are presented. The concentrations of the methylene chloride, methyl ethyl ketone, and trichloroethane at the condenser vent were much greater at the beginning of the process than at the middle of the process. The observed concentration results from the vapor of the waste being charged into the stripper being forced up the condenser vent. This is not unexpected since the concentrations of these components are much greater at the beginning of the cycle than at midcycle, as seen in Tables 34 and 35. Even more importantly, the concentrations for MEK and TCEA correspond very well with those at t=0 in headspace analysis (Table 38). The concentrations of VOCs in the product storage vent and the MST vent were substantially lower than the concentrations obtained at equilibrium within the storage tank.

Table 45 estimates the air emissions on the basis of the average of the results of the tests on the air samples taken from the second batch. The volume emitted from the condenser vent was estimated on the basis of the data obtained from the integrated flow as determined by dry gas meter readings (Allen, 1985d). In Batch 2 (1,1,1-trichloroethane/oil) a gas flow of 179 liters was monitored over a 47-minute period; the average gas flow was 3.8 L/min. Two air samples were taken from the condenser vent during the midcourse of the process. One condenser vent sample was taken during batch

TABLE 44. AIR EMISSIONS ESTIMATIONS: BATCH 1 (Aqueous Xylene)

	Volume[a]	Component	Concentration[b] (mg/L)	Total Emissions[c] (g)
Condenser vent	790 L	Methyl ethyl ketone	7.7	6.1
Condenser vent	790 L	Isopropyl alcohol	1.9	1.5
Condenser vent	790 L	1,1,1-Trichloroethane	1.8	1.4
Condenser vent	790 L	Tetrachloroethene	0.98	0.77
Condenser vent	790 L	Ethyl benzene	1.6	1.3
Condenser vent	790 L	Toluene	6.7	5.3
Condenser vent	790 L	Xylene	3.5	2.8
		Total VOC emissions		19.2
Emission factor (g/g waste treated)[d]			1.5×10^{-5}	
Emission factor (g/g VOC removed)[e]			5.7×10^{-5}	

[a] 683 L/108 min x 125 min = 790 L. (See text)

[b] Average of condenser vent concentrations in Table 36.

[c] Product of concentration and volume.

[d] 1.26 Mg waste fed to process.

[e] 333 kg solvent recovered.

TABLE 45. AIR EMISSIONS ESTIMATIONS: BATCH 2
(1,1,1-Trichloroethane/Oil)

Time (min)	Volume	Component	Concentration (mg/L)	Emissions[a] (g)
46-47	391 L[b]	Methyl ethyl ketone	1.36[c]	0.53
46-47	391 L[b]	1,1,1-Trichloroethane	54[c]	21.1
Total VOC Emissions			21.6 g	
Emission factor (g/g waste treated)[d]			2.0×10^{-5}	
Emission factor (g/g VOC removed)[e]			2.7×10^{-5}	

[a] Product of concentration and Volume.
[b] 103 min x 3.8 L/min = 391 L (see text).
[c] Average of measurements at 46 and 47 minutes (see Table 37).
[d] 1,100 kg waste basis.
[e] 800 kg VOC basis.

heating. Initially, the concentrations of the VOCs were substantially greater than during process mid-cycle (factor of 10 or greater). The volume of gas emitted during the initial heating is assumed to equal the batch size. These initial emissions were not used to estimate the emissions because of the lack of measured gas flow rates during the initial period.

The emission factors were estimated by obtaining the ratio of the estimated grams of emissions to the total amount of wastes charged into the system and the total amount of volatile materials recovered. Emission rates are calculated by obtaining the ratio of the grams emitted to the process time (sec). The data that were used in the calculations are presented in Table 45. The emission rate was 0.0035 g/sec for the 1,1,1-trichloroethane production Batch 2. This value should be used with care in health effects calculations using emission rates since the rate does not necessarily apply to other waste streams and it does not reflect process downtime. The emission factors in terms of g/g waste are expected to be more appropriate for dispersion modeling calculations. In both Batches 1 and 2 tested, emissions were only a small fraction of the VOCs recovered from the process, thus suggesting that the use of waste treatment does not itself produce significant emissions.

In contrast to the open product storage tank at Plant C, the product storage vessels at Plant D were enclosed inside a building with a vent to the roof from each tank. The flow rates from the vents of the product-receiving vessel and the separator could not be measured with an Alnor velometer because of the very low flow rates. Since the flow rate was not measurable with the velometer (less than 25 cm/sec), the volume of the displaced gas was multiplied by the concentration measured in the gas to estimate the VOCs lost. The rates estimated from concentrations and working losses in the storage tank and MST are 0.4 mg/sec and 2.4 mg/sec, respectively. These air emissions from the storage tanks at Plant D were much lower than from the storage tank surface exposed to the flow of air at Plant C.

Liquid Residuals

The condensed steam and organics are collected in a receiving vessel and the liquid is transferred to a decanter. The recovered organic layer is transferred to a product storage tank. Some solvents can be sold as paint thinners or cleaners; the 1,1,1-trichloroethane can be sold as a specialty solvent if stabilized to avoid hydrochloric acid decomposition. Recovered solvents (nonhalogenated) can be used as fuel or fuel supplements. The condensed steam containing VOCs is steam stripped to remove the VOCs so that the treated water can be sent to a public waste water treatment facility. Batch 3 was an example of how the VOCs could be removed from the condensed steam used in treating an organic waste. If the treated waste has sufficient Btu content (e.g., Batch 2), then it can be burned as fuel after the chlorinated material is removed. Aqueous residues from the stripper are currently being solidified and landfilled.

PROCESS COST

General Facility Costs for Plant D

This section describes cost information provided by Plant D during the pretest site survey. The cost per unit volume is dependent on the size of the unit and the volumetric throughput, as well as the type of waste. The condensed steam also needs to be treated and this will decrease the throughput.

Capital Cost (New Unit, 1984)--

DCI Steam Stripping System	$80,000
Support Facilities and Installation (building, tanks, boiler, air compressor, cooling water tower, pumps, lines)	$370,000
Total Installed	$450,000

Operating Cost (1984)--

Salaries and Payroll Tax	$ 6,000/mo.
Maintenance	800/mo.
Material and Supplies	4,000/mo.
Fuel, Utilities	5,000/mo
Monthly Operating Cost	$ 15,800
Annualized	$189,600

Total Annualized Cost--

Annual Operating Cost	$189,600
Capital Recovery Factor (10 percent over 1 year)	73,300
Total	$262,900

Process throughput for the steam stripping system was reported to range from 130 L/hr (35 gal/hr) to 760 L/hr (200 gal/hr) depending upon the characteristics of the stream being processed. This throughput does not include treating the residuals which are produced, but can be used to determine to a first approximation the range of waste processing costs.

1. At 130 L/hr (35 gal/hr), 24 hr/day, 5 days per week:

Total Waste Processed (L/yr)	824,000	
(gal/yr)	218,000	
Total Annualized Cost		$262,900
Unit Cost ($/L)		$ 0.319
($/gal)		$ 1.206

2. At 760 L/hr (200 gal/hr), 24 hr/day, 5 days per week:

Total Waste Processed (L/yr)	4,723,680	
(gal/yr)	1,248,000	
Total Annualized Cost		$262,900
Unit Cost ($/L)		$ 0.056
($/gal)		$ 0.211

Unit Treatment Costs for Each Batch

The unit costs of treating each of the four waste batches were estimated and are presented in Table 46, along with unit solvent recovery costs. The purpose of this analysis was to determine the cost-effectiveness of steam stripping these four streams to remove VOCs and to determine if any conclusions could be drawn about the influence of waste type, batch size, degree of treatment, or initial waste VOC content on unit costs.

The annual process operating costs used in this calculation was assumed to be that derived above ($262,900). The amount of waste which could be treated in a year varied from batch to batch. This annualized waste volume was dependent upon the volume of waste charged to the system and the time it took to process the waste (i.e., the batch cycle time). The annualized waste volume that could be treated in the system was estimated as the batch size times the ratio of the annual process time (24 hours per day, 5 days per week, 52 weeks per year) to the batch process time. The batch cycle time was taken to be equal to the sum of (1) the waste stripping time (derived from batch process data, Appendix B); (2) an assumed 40 minutes for emptying and recharging the unit, and for heating each batch; and (3) the time required to strip the VOC from the MST condensate that was produced by the stripping. The derivation of the condensate stripping time is provided in Appendix E.

The volume of solvent recovered in a batch run was taken to be the organics removed from the waste. It was the difference between the products of the waste VOC concentration and waste volume before and after stripping. The annualized solvent recovery was calculated from the product of the annualized waste volume and the ratio of solvent recovery to batch size.

Unit waste treatment and solvent recovery costs were obtained by dividing the annual operating cost by the annualized waste volume and solvent recovered volume, respectively.

A sample calculation showing the derivation of a unit treatment cost is provided in Appendix F.

Because each of these batches has different initial VOC content and volume and has undergone different degrees of treatment (i.e., percent VOC removed), conclusive statements cannot be made from Table 46 about the factors influencing treatment cost. However, several qualified conclusions can be drawn. Compared to mixed aqueous Batch 1, organic Batch 2 has a charge that is lower by approximately 30 percent and has a greater initial VOC concentration (see Table 28). Yet, the unit treatment cost for Batch 2 is 20

TABLE 46. ESTIMATED UNIT COST FOR THE FOUR BATCHES TESTED

Waste stream	Aqueous xylene	1,1,1-Trichloroethane	Aqueous 1,1,1-trichloroethane	Aqueous mixed solvent
Waste volume, liters	1,590	897	564	360
(gallons)	(420)	(237)	(149)	(95)
Organic solvent recovery, liters	333	660	95	11
(gallons)	(88)	(174)	(25)	(3)
Condensate stream, liters	359	393	256	1,320
(gallons)	(95)	(104)	(68)	(35)
Condensate treatment cost \$/liter[a]	0.01	0.05	0.06	0.06
Batch cycle time, hours[b]	2.35	2.48	1.88	1.30
Process rate (L/hr)	677	362	300	276
Annualized waste volume, liters[a]	4,224,000	2,259,000	1,872,000	1,725,000
(gallons)	(1,116,000)	(596,700)	(494,500)	(455,700)
Annualized solvent recovery, liters[a]	885,024	1,662,000	314,500	52,800
(gallons)	(233,793)	(439,100)	(83,100)	(13,900)
Total annual operating cost, \$[a]	262,900	262,900	262,900	262,900
Cost per unit volume:[a]				
1) Waste treatment, \$/liter	0.06	0.12	0.14	0.15
\$/gallon	(0.236)	(0.44)	(0.53)	(0.58)
2) Solvent recovery, \$/Mg	345	119	629	5,242
\$/liter VOC	0.324	0.166	0.147	0.156

[a] The method of calculation is presented in Appendix E.

[b] The stripping time plus 40 minutes plus time to treat the condensate.

percent lower than for Batch 1. It is believed that this is due to the fact that the stripping rate constants for VOC compounds in organic matrices are higher than for compounds in waste, as is indicated for methyl ethyl ketone and trichloroethane in Table 41.

While waste treatment unit costs vary by less than a factor of two among the four batches, solvent recovery unit costs vary by over an order of magnitude. Much higher costs are incurred for Batches 3 and 4 due to both a small initial batch size and their lower initial VOC contents.

Variation of Unit Costs With Degree of Treatment

The extent to which solvent recovery and waste treatment costs are influenced by the degree of treatment (i.e., percent of VOC removed) was investigated. The analysis was performed on each of the four batches to determine unit costs for reducing VOC content of wastes by from 68.4 percent to 99.9 percent. The results of the cost analyses are presented in Tables 47-50. The costs per unit weight ($/Mg) recovered solvent that were derived in these tables are presented graphically in Figures 30-33.

As with the previous analysis (Table 45), the present analyses used the batch charge volumes and initial VOC concentrations as observed in the field. The volume of organic solvent recovered was determined by percent VOC removed (and solvent density, see Table E-1). The amount of steam condensate that was produced during the stripping and the resultant time and costs associated with condensate treatment were also handled in a similar manner (see Appendix E) and were accounted for in determining the batch cycle times and, then, the waste processing rate. As with the analysis in Table 46, a 24-hour-per-day, 5-day-per-week operating schedule was assumed when calculating annualized waste volumes and annualized solvent recovery volumes.

Several additional elements were added to the cost analysis presented in Tables 47-50, compared to the Table 46 analysis. First, a stripping rate constant which was representative of the total VOC component of the waste had to be derived so that the variation in VOC content with time could be estimated. Second, the analysis accounted for:

a. the variation in steam load (and cost) with batch cycle time.

b. waste processing credits, i.e., the income that a recycler received for acquiring waste.

c. variation in treatment residual disposal costs with composition of the residual.

d. income from sale of the recovered solvent.

The approaches to determining a representative stripping constant and to estimating the steam load are complex and are presented in Appendix E. The waste processing credits was assumed to be equal to the landfilling costs incurred by Plant D, approximately $0.37 per liter. (In fact, the facility typically charges from $0.50/liter ($100/drum) for waste received by the

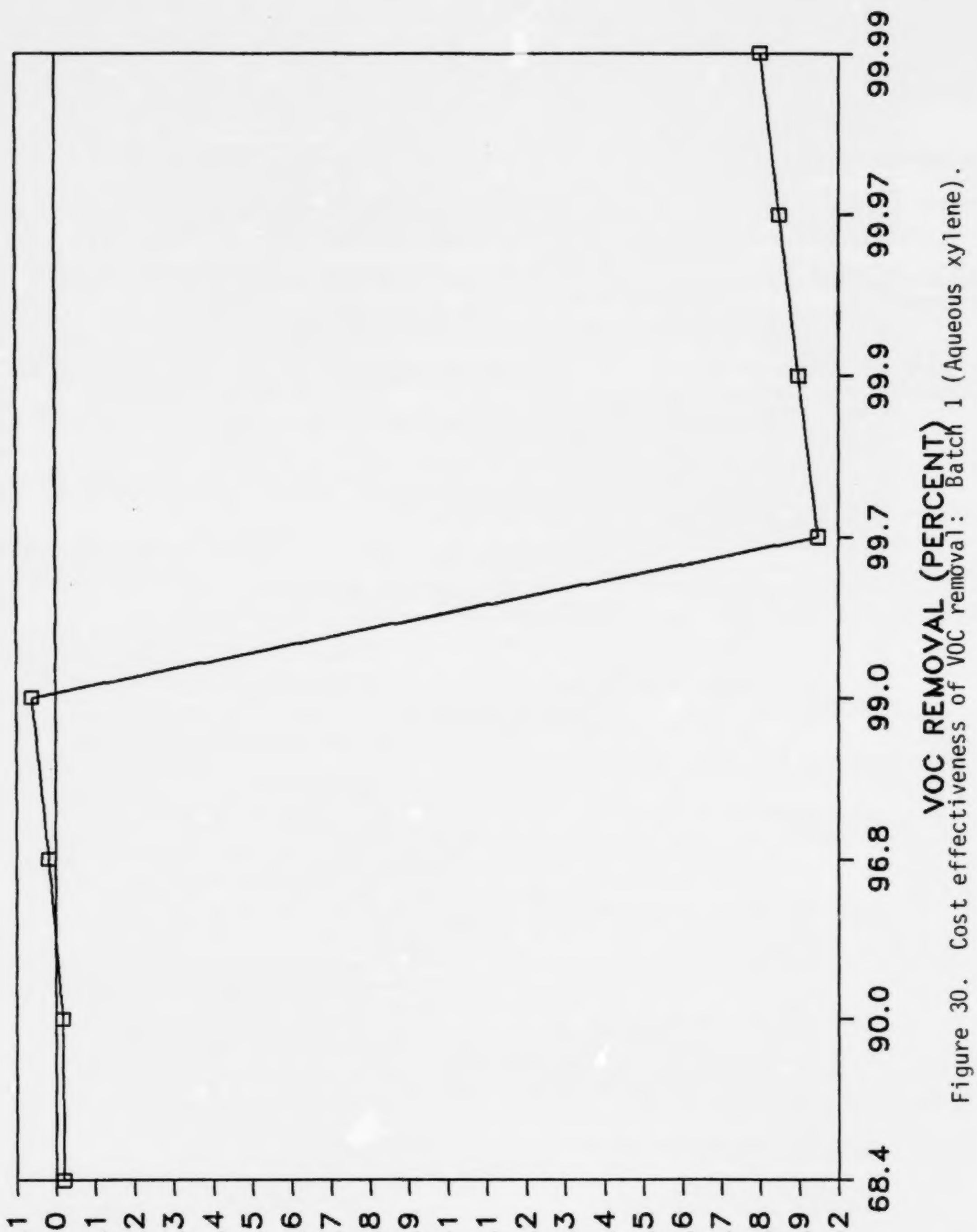


Figure 30. Cost effectiveness of VOC removal: Batch 1 (Aqueous xylene).

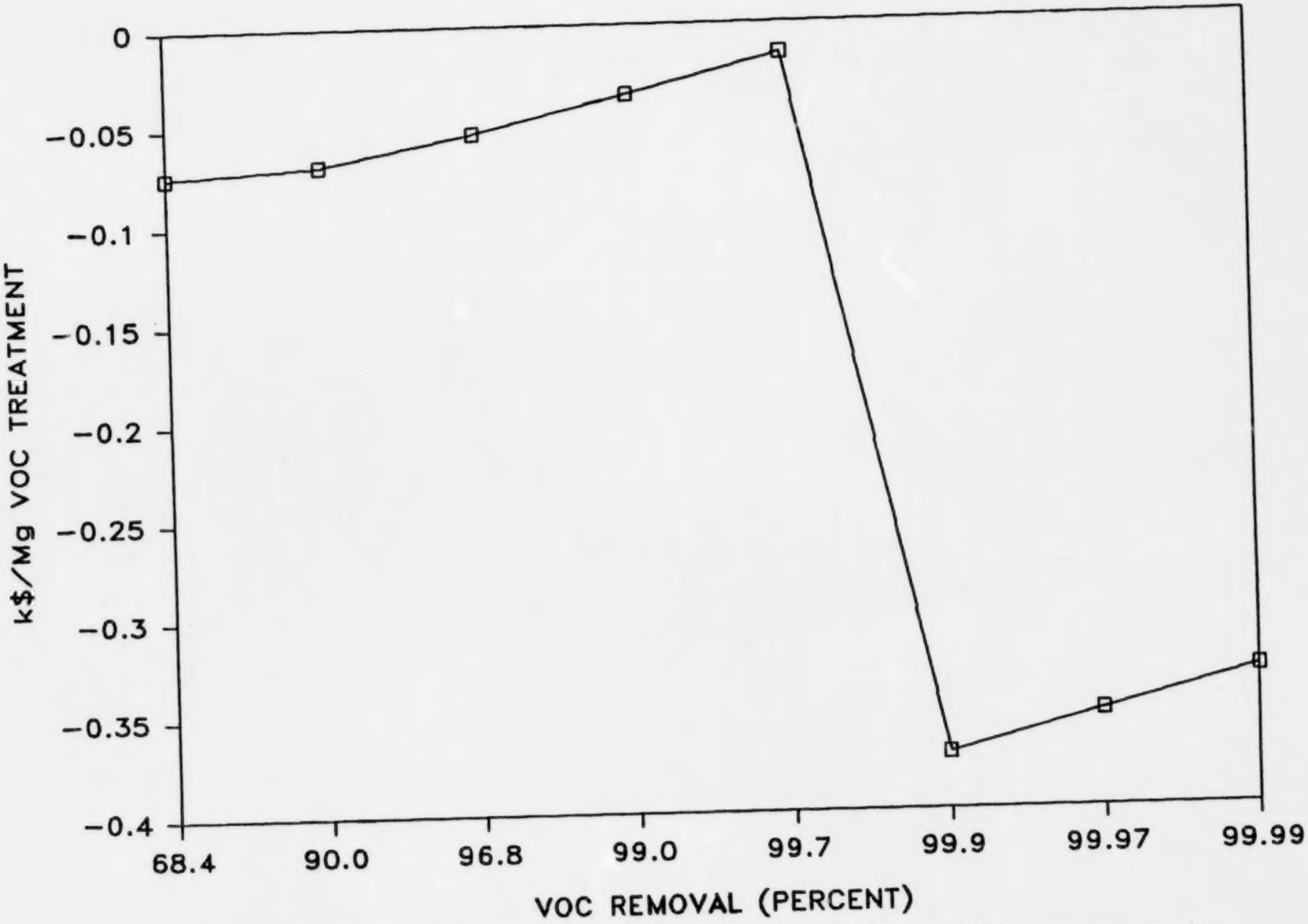


Figure 31. Cost effectiveness of VOC removal: Batch 2 (1,1,1-trichloroethane/oil).

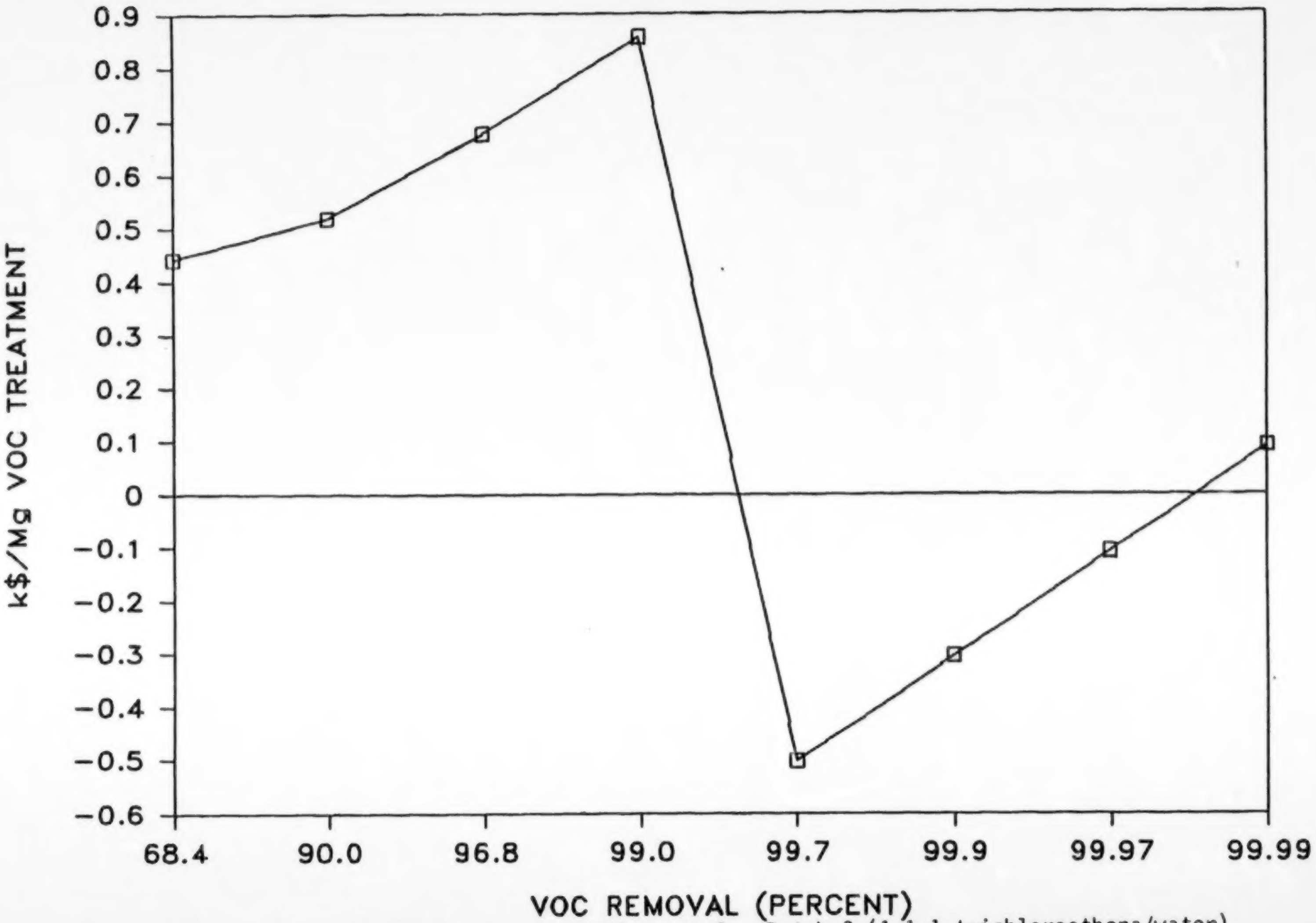


Figure 32. Cost effectiveness of VOC removal: Batch 3 (1,1,1-trichloroethena/water).

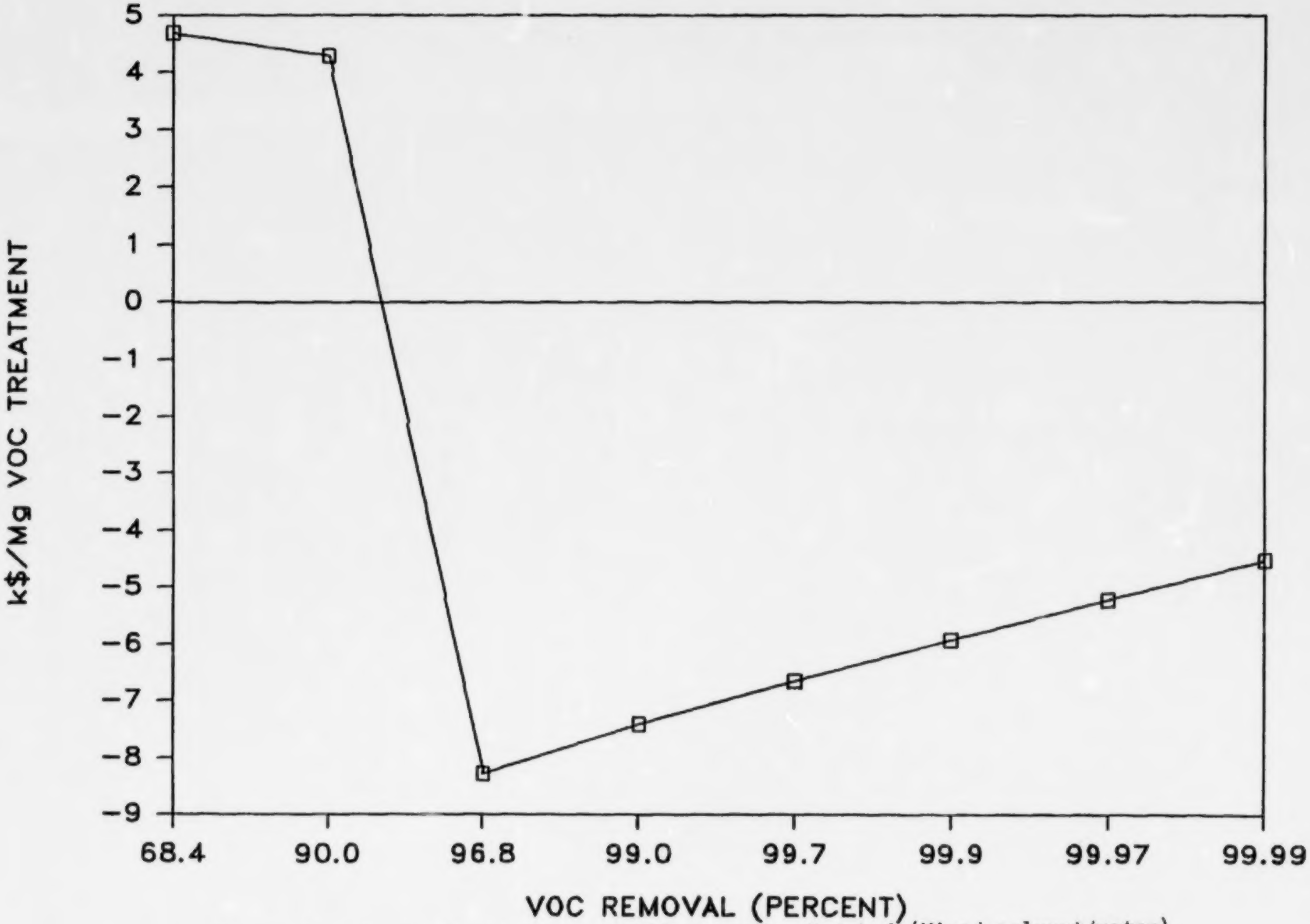


Figure 33. Cost effectiveness of VOC removal: Batch 4 (Mixed solvent/water).

TABLE 47. COST ANALYSIS FOR THE DIRECT STEAM STRIPPING OF HAZARDOUS WASTE: BATCH 1 (AQUEOUS XYLENE)

	Percent VOC removal					
	68.4	90.0	96.8	99.0	99.7	99.9
Concentration of residual VOC	6.636	2.1	0.6636	0.21	0.06636	0.021
Waste volume (L)	1590	1590	1590	1590	1590	1590
Organic solvent recovery (L)	228	301	323	331	333	334
Steam condensate (L)	68.4	136.7	205.1	273.4	341.8	410.0
Condensate treatment time (min.)	3.5	6.9	10.4	13.9	17.3	20.8
Condensate treatment ($/L waste)	($0.01)	($.00)	$0.01	$0.01	$0.01	$0.02
Batch cycle time (min.)	56	72	87	103	119	135
Processing rate (L/hr)	1610	1216	976	816	701	614
Annualized waste volume (L)	9974093	7502739	6011388	5015653	4302146	3766946
Annualized solvent recovery (L)	1432679	1418018	1222500	1042754	900596	790268
Total annual operating cost	$262,900	$262,900	$262,900	$262,900	$262,900	$262,900
Waste collection revenues ($)						
at $0.37 /L	3690415	2776013	2224214	1855791	1591794	1393770
Solvent sale credits ($)						
at $0.20 /L	286536	283604	244500	208551	180119	158054
Treated waste disposal costs ($)						
0.10% or more VOC landfilled	$3,690,415	$2,776,013	$2,224,214	$1,855,791	$215	$188
Waste processing cost	($23,636)	($20,704)	$18,400	$54,349	($1,508,798)	($1,288,735)
Cost per unit volume:						
waste treatment ($/L)	($.00)	($.00)	$.00	$0.01	($0.35)	($0.34)
solvent recovery ($/L)	($0.02)	($0.01)	$0.02	$0.05	($1.68)	($1.63)
solvent recovery ($/Mg)	($19)	($17)	$18	$61	($1,948)	($1,896)
Incremental cost ($/L solvent)	($0.02)	($0.01)	$0.41	$1.71	($251.70)	$18.94
Waste residual volatility, torr	116.76	36.95	11.68	3.69	1.17	0.37
VOC landfilled with treated waste	31.600%	10.000%	3.160%	1.000%	0.000%	0.000%
VOC sent to POTW with treated waste	0.000%	0.000%	0.000%	0.000%	0.316%	0.100%

( ) indicates credit.

TABLE 48. COST ANALYSIS FOR THE DIRECT STEAM STRIPPING OF HAZARDOUS WASTE: BATCH 2 (1,1,1-TRICHLOROETHANE)

	Percent VOC removal					
	68.4	90.0	96.8	99.0	99.7	99.9
Concentration of residual VOC	23.384	7.4	2.3384	0.74	0.23384	0.074
Waste volume (L)	897	897	897	897	897	897
Organic solvent recovery (L)	454	597	643	657	662	663
Steam condensate (L)	87.0	174.0	261.0	347.9	435.0	521.9
Condensate treatment time (min.)	4.9	9.8	14.7	19.6	24.5	29.4
Condensate treatment ($/L waste)	($0.04)	$.00	$0.03	$0.06	$0.09	$0.12
Batch cycle time (min.)	59	78	98	117	136	155
Processing rate (L/hr)	840	610	479	395	335	292
Annualized waste volume (L)	5107651	3671502	2864941	2349455	1990803	1727434
Annualized solvent recovery (L)	2585288	2445220	2053063	1721211	1468539	1277023
Total annual operating cost	$262,900	$262,900	$262,900	$262,900	$262,900	$262,900
Waste collection revenues ($)						
at $0.37 /L	1889831	1358456	1060028	869298	736597	639151
Solvent sale credits ($)						
at $0.20 /L	517058	489044	410613	344242	293708	255405
Treated waste disposal costs ($)						
0.10% or more VOC landfilled	$1,889,831	$1,358,456	$1,060,028	$869,298	$736,597	$86
Waste processing cost	($254,158)	($226,144)	($147,713)	($81,342)	($30,808)	($631,569)
Cost per unit volume:						
waste treatment ($/L)	($0.05)	($0.06)	($0.05)	($0.03)	($0.02)	($0.37)
solvent recovery ($/L)	($0.10)	($0.09)	($0.07)	($0.05)	($0.02)	($0.49)
solvent recovery ($/Mg)	($74)	($70)	($54)	($36)	($16)	($372)
Incremental cost ($/L solvent)	($0.10)	($0.07)	$0.20	$1.06	$3.78	($219.05)
Waste residual volatility, torr	13.33	4.22	1.33	0.42	0.13	0.04
VOC landfilled with treated waste	31.600%	10.000%	3.160%	1.000%	0.316%	0.000%
VOC sent to POTW with treated waste	0.000%	0.000%	0.000%	0.000%	0.000%	0.100%

( ) indicates credit.

TABLE 49. COST ANALYSIS FOR THE DIRECT STEAM STRIPPING OF HAZARDOUS WASTE: BATCH 3 (AQUEOUS 1,1,1-TRICHLOROETHANE)

	Percent VOC removal					
	68.4	90.0	96.8	99.0	99.7	99.9
Concentration of residual VOC	5.688	1.8	0.5688	0.18	0.05688	0.018
Waste volume (L)	564	564	564	564	564	564
Organic solvent recovery (L)	69	91	98	101	101	101
Steam condensate (L)	108.8	217.5	326.3	434.9	543.7	652.4
Condensate treatment time (min.)	7.0	13.9	20.9	27.9	34.8	41.8
Condensate treatment ($/L waste)	$0.03	$0.11	$0.22	$0.37	$0.55	$0.77
Batch cycle time (min.)	64	88	112	136	160	184
Processing rate (L/hr)	477	332	255	207	174	150
Annualized waste volume (L)	2708942	1822681	1372944	1101496	919476	789222
Annualized solvent recovery (L)	333525	295274	239321	196287	164983	141918
Total annual operating cost	$262,900	$262,900	$262,900	$262,900	$262,900	$262,900
Waste collection revenues ($)						
at $0.37 /L	1002309	674392	507989	407553	340206	292012
Solvent sale credits ($)						
at $0.20 /L	66705	59055	47864	39257	32997	28384
Treated waste disposal costs ($)						
0.10% or more VOC landfilled	$1,002,309	$674,392	$507,989	$407,553	$46	$39
Waste processing cost	$196,195	$203,845	$215,036	$223,643	($110,257)	($57,456)
Cost per unit volume:						
waste treatment ($/L)	$0.07	$0.11	$0.16	$0.20	($0.12)	($0.07)
solvent recovery ($/L)	$0.59	$0.69	$0.90	$1.14	($0.67)	($0.40)
solvent recovery ($/Mg)	$442	$519	$676	$857	($502)	($304)
Incremental cost ($/L solvent)	$0.59	$1.01	$3.64	$11.94	($262.30)	$121.17
Waste residual volatility, torr	2.33	0.74	0.23	0.07	0.02	0.01
VOC landfilled with treated waste	31.600%	10.000%	3.160%	1.000%	0.000%	0.000%
VOC sent to POTW with treated waste	0.000%	0.000%	0.000%	0.000%	0.316%	0.100%

( ) indicates credit.

TABLE 50. COST ANALYSIS FOR THE DIRECT STEAM STRIPPING OF HAZARDOUS WASTE: BATCH 4 (MIXED AQUEOUS)

	Percent VOC removal					
	68.4	90.0	96.8	99.0	99.7	99.9
Concentration of residual VOC	0.9796	0.31	0.09796	0.031	0.009796	0.0031
Waste volume (L)	360	360	360	360	360	360
Organic solvent recovery (L)	8	10	11	11	11	11
Steam condensate (L)	34.9	69.8	104.7	139.6	174.5	209.3
Condensate treatment time (min.)	1.4	2.7	4.1	5.5	6.8	8.2
Condensate treatment ($/L waste)	$0.01	$0.03	$0.05	$0.08	$0.12	$0.16
Batch cycle time (min.)	49	57	66	75	84	92
Processing rate (L/hr)	431	359	307	269	239	215
Annualized waste volume (L)	2665911	2205833	1880836	1639571	1452959	1304652
Annualized solvent recovery (L)	56528	61543	56463	50318	44899	40404
Total annual operating cost	$262,900	$262,900	$262,900	$262,900	$262,900	$262,900
Waste collection revenues ($)						
at $0.37 /L	986387	816158	695909	606641	537595	482721
Solvent sale credits ($)						
at $0.20 /L	11306	12309	11293	10064	8980	8081
Treated waste disposal costs ($)						
0.10% or more VOC landfilled	$986,387	$816,158	$94	$82	$73	$65
Waste processing cost	$251,594	$250,591	($444,208)	($353,723)	($283,602)	($227,837)
Cost per unit volume:						
waste treatment ($/L)	$0.09	$0.11	($0.24)	($0.22)	($0.20)	($0.17)
solvent recovery ($/L)	$4.45	$4.07	($7.87)	($7.03)	($6.32)	($5.64)
solvent recovery ($/Mg)	$4,685	$4,286	($8,281)	($7,400)	($6,649)	($5,936)
Incremental cost ($/L solvent)	$4.45	$2.87	($164.96)	$30.52	$96.92	$306.98
Waste residual volatility, torr	22.84	7.23	2.28	0.72	0.23	0.07
VOC landfilled with treated waste	31.600%	10.000%	0.000%	0.000%	0.000%	0.000%
VOC sent to POTW with treated waste	0.000%	0.000%	3.160%	1.000%	0.316%	0.100%

( ) indicates credit.

truckload to $1.00/liter ($200/drum) for smaller loads, making this credit conservatively low.)

At Plant D, wastewaters which contain less than 0.1 percent organics can be discharged to the municipal treatment system. The cost for this is approximately $0.0005 per liter, and this figure was assumed to be the cost for stripper bottoms disposal in the cost analysis when treatment was sufficient to reach this level. For bottoms containing over 0.1 percent organics, it was assumed that the bottoms were sent to a landfill at a cost of $0.37 per liter.

From Tables 37-40 and Figures 30-33, the following conclusions can be drawn. The figures of the VOC treatment costs as a function of the percent VOC removal show a dramatic decrease in cost when the residual waste can be disposed by sewer to a publicly-owned wastewater facility, instead of landfilling; it is assumed that wastes containing less than 0.1 percent VOC can be sent to a sewer. The cost of disposal by sewer is substantially less than landfilling costs. This analysis suggests that disposal costs and revenues for waste collection are major components of the cost analysis. The cost of VOC removal adds to the costs, particularly at high VOC removal rates. The treatment of organic wastes (Batch 2) is estimated to be more profitable than for aqueous wastes (Batches 1, 3, and 4).

SECTION 9

FIELD TEST RESULTS: DISTILLATION

This section describes the field evaluation at Plants B and E. The distillation system at Plant B differs from the direct injection system at Plant D in that the capacity of Plant B is larger, the steam heats the waste indirectly through coils, and the stream of vapors is processed in a distillation column.

Distillation to treat hazardous waste was investigated since low concentrations of VOCs in water can be removed and recovered as an organic stream. In batch distillation, the batch can be treated until the concentrations of VOCs are below specifications. Organic materials can be recovered with distillation which have significant water solubilities; with steam stripping, a mixture of water and organic would be obtained from the process and would require further processing.

DISTILLATION FIELD EVALUATION AT PLANT B

Process Description

Contaminated organic chemicals and solvents are received in bulk and drum shipments and processed for reclamation and recycle. All waste material is either processed in the thin film evaporator or the kettles. Approximately 90 percent of the incoming shipments are processed through one of two Votator thin-film evaporators during which about 80 percent of the material is stripped off as overhead product. The overhead product may or may not be further refined through fractionation distillation, depending upon the intended end use. Distillation bottoms are shipped offsite and utilized as fuel in cement kilns. There is an additional discussion of Plant B wastes and processes in Section 7.

There are eight fractionation distillation systems of varying capability and capacity at the Plant B facility. The fractionation distillation systems each consist of a reboiler, a tray column and condenser, an accumulator, and associated pumps, valves, and piping (Figure 34). Instrumentation includes a reboiler and column head vapor temperature recorders (multipoint recorder) and rotameters in the reflux and product lines. The system selected for any particular separation is dependent upon a number of factors such as throughput, relative vapor pressures, and required purity of the process streams.

Aqueous phases from distillation operations may be disposed of in a municipal wastewater treatment facility if the organic concentration is less than 0.1 percent by weight; otherwise it is shipped offsite for treatment and

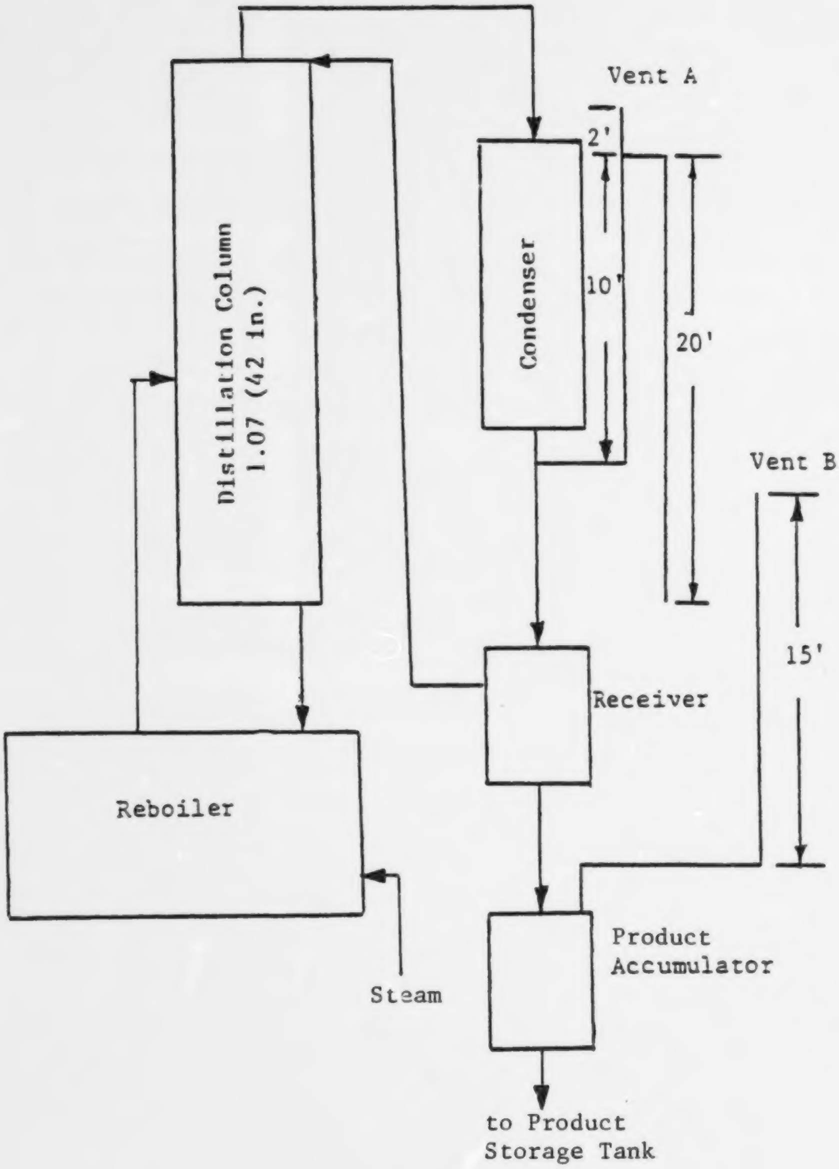

Distillation Column
1.07 (42 in.)
Vent A
2'
10'
20'
Condenser
Vent B
15'
Receiver
Reboiler
Steam
Product
Accumulator
to Product
Storage Tank

Figure 34. Distillation process: Batch 1 (Aqueous MEK).

disposal. Still bottoms which are unacceptable for fuel are sent to a landfill.

The reboiler contains a steam coil for heating. The steam supply header pressure is controlled at 125 psig, but there is some fluctuation in pressure, due to the nature of the controller. Steam flow is controlled manually by the operator with a hand valve.

The fractionation column is a tray column. Vapor from the reboiler enters about midway up the column, and the bottoms from the column recycles back to the reboiler by gravity. Reflux is provided to the top of the column from the accumulator by a small centrifugal pump. The reflux flow rate is controlled manually with a hand valve by the operator.

The overhead condenser is a vertical, shell-and-tube, water-cooled condenser. The distillate accumulator (approximately 50 L) is a small tank from which the column reflux is pumped, with the product overflowing to any of a number of product storage tanks.

A typical operation involves charging a quantity of material to the reboiler. The quantity is noted from visual observation of the liquid level in the reboiler. Steam is then applied to the coil in the reboiler, and the batch is heated up with the column operating under total reflux. After the reboiler and column head temperatures have been lined out, the steam flow and reflux are set and product takeoff is started. The distillation is continued until such time as the column head temperature begins to rise indicating that the volatile component being stripped from the batch is essentially depleted. The process may either be discontinued at this time or, as is done with some aqueous streams, stripping may be continued in order to achieve a VOC level of less than 0.1 percent for disposal as waste water. In the case of the latter, laboratory analyses are run periodically to determine the VOC content.

The steam flow rate to the reboiler and the reflux rate to the column are controlled by an operator through manual adjustment of hand valves. The column head and reboiler temperatures and the distillate rate and appearance are the primary factors used in control of the process.

The distillate condenser is vented to the atmosphere where emissions should be mostly noncondensibles. However, this is a potential source of VOC emissions should the condenser become overloaded for any reason. The reflux accumulator is also vented to the atmosphere, and emissions from this tank would represent operational displacement of equilibrium vapor from the distillate.

Process Effectiveness

Two different waste streams were selected for the field evaluation at Plant B. A summary of the waste characterization and process data is presented in Table 51. The individual components in these two waste streams are characterized in Tables 52 and 53. The waste streams were both aqueous organic and consisted primarily of methyl ethyl ketone and acetone, respectively. These wastes were obtained directly from the generator. The

TABLE 51. DISTILLATION WASTE CHARACTERIZATION AND PROCESS DATA

	Batch 1	Batch 2
Initial volume (L)[a]	30,000	11,400
VOC (mass percent)[a]	4.7	23
Water content[a]	95	77
Process Data		
Distillation time[a]	13.5 hr	8.0 hr
Steam rate (kg/hr)[b]	860	615
Stripper residue volume (L)	28,500	8,800
Bottoms VOC content (weight %)[c]	0.05	0.07
VOC recovered (kg)[a]	1,400	2,614
% VOC recovered[a]	99	99.8

[a] Measured

[b] Estimated.

[c] Estimated by material balance.

TABLE 52. WASTE CHARACTERIZATION OF BATCH 1
(Aqueous Methyl Ethyl Ketone)

Total solids (mg/L)	340
pH	5.5
Water (weight percent)	95
Oil (weight percent)	Negligible
VOC (weight percent)	5
Density (g/cm^3)	1
Number of phases	1

VOC analysis (Aqueous phase)

Compound	Concentration (mg/L)
Methyl ethyl ketone	30,000
2,2-Dimethyl oxirane	6,400
Isopropanol	1,900
Methylene chloride	3,100
Methanol	3,500
Carbon tetrachloride	1,700
1,1,1-Trichloroethane	710
Other VOCs	2,130

TABLE 53. WASTE CHARACTERIZATION OF BATCH 2
(Aqueous Acetone)

Total solids (mg/L)	7,500
pH	13
Water (weight percent)	77
Oil (weight percent)	Negligible
VOC (weight percent)	23
Density (g/cm^3)	1
Number of phases	1

VOC analysis (Aqueous phase)

Compound	Concentration (mg/L)
Acetone	212,000
Trichloroethene	9,500
1,1,1-Trichloroethane	2,800
Toluene	2,700
Methyl ethyl ketone	2,300
Isopropanol	440
Aromatics	291

objectives in processing these wastes were to reclaim solvent and reduce the VOC content to a level acceptable for disposal in a municipal wastewater treatment facility. However, due to some light sludge, oil, or heavy organic contamination in the acetone stream as received, it was unlikely that the residue from this batch could be made acceptable for disposal to the sewer and was sent to Plant F for disposal.

Two distillation systems having the same design but different reboiler capacities and column diameters were used.

Process data collected during processing included reboiler temperature, column head temperature, reflux rate, and in one case product rate (see Appendix B). There were no means to measure the steam flow to the reboiler during distillation, but approximate rates could be obtained by enthalpy calculations. The quantity of distillate recovered could not be measured since there were no liquid level instruments on the product storage tanks. These tanks were very large, on the order of 37,850 liters (10,000 gallons) or greater, and in both cases contained product from previous batches.

Methyl Ethyl Ketone Batch--

A 30,280-liter (8,000-gallon) batch of the methyl ethyl ketone (MEK) waste stream was charged to the reboiler of a 42-inch (110-cm) system (designated by column diameter). This is a 41,635-liter (11,000-gallon) reboiler, and the column in this system has 30 trays. The 41,635-liter charge was determined by visual observation of the level in the reboiler by an operator.

The column was operated under total reflux during the heatup which lasted until the reboiler and column head temperatures were lined out (became constant). The system was held under total reflux for about 1 hour before distillation was started. The reboiler and column head temperatures and the rate of distillate flow were monitored to determine the progress of the distillation. The distillation was essentially completed when the reboiler temperature had reached 100°C and a rapid rise in the column head temperatures occurred, indicating depletion of the MEK. However, stripping was continued until a VOC level of less than 0.1 percent was achieved as evidenced by Plant B laboratory analyses. The aqueous residue remaining in the reboiler was then discharged to the sewer for processing through the municipal wastewater treatment system.

The overhead product was put into a tank in which organic distillate was being accumulated for further refining prior to being returned to a specific client.

Acetone Batch--

The 32-inch (81-cm) distillation system (designated by column diameter) was used for processing this batch. This system includes a 13,248-liter (3,500-gallon) reboiler and has 30 trays (Figure 35).

An 11,335-liter (3,000-gallon) batch of the acetone waste stream was charged to the reboiler. The column was operated under total reflux during the period of heatup and until the reboiler and column head temperatures had

0.81M (32 in.) Distillation Unit

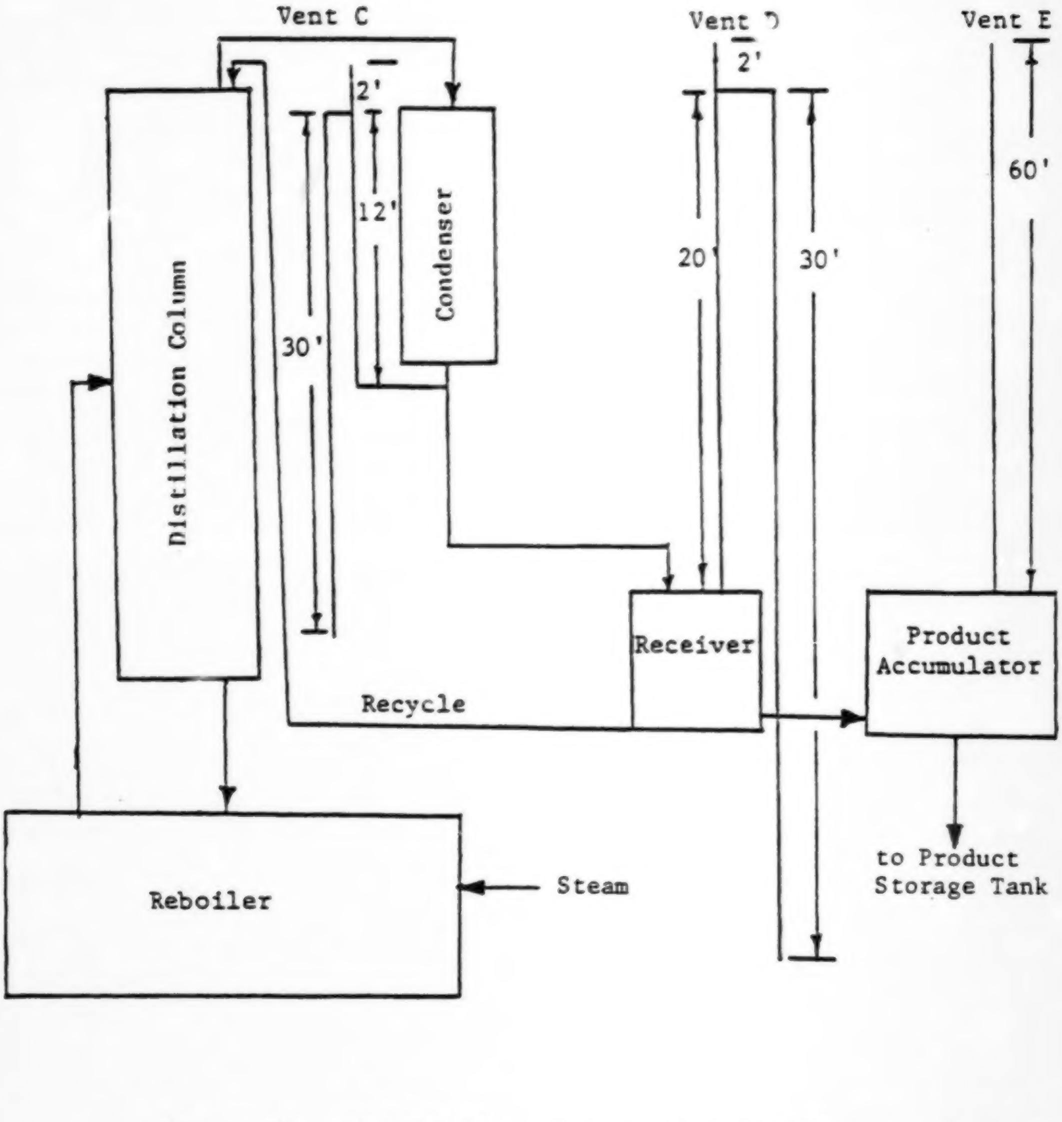

Vent C
Vent D
Vent E
2'
2'
12'
30'
20'
30'
60'
Distillation Column
Condenser
Receiver
Product Accumulator
Recycle
Reboiler
Steam
to Product Storage Tank

Figure 35. Distillation process: Batch 2 (Aqueous acetone).

lined out. The system was held at this condition for about 3-1/2 hours prior to the start of distillation only for scheduling purposes. The reboiler and column head temperatures and the distillate rate were monitored during processing to determine the progress of the distillation.

This waste stream contained some contamination of heavy organics or light sludge as received. The aqueous residue would normally have been stripped to a level acceptable for disposal to the sewer, but the unexpected contamination precluded this option. Therefore, the distillation was completed after the batch temperature had reached 100°C and the column head temperature began to rise rapidly indicating depletion of the organic solvent. The final batch sample was taken at that time.

The distillate was put into a tank in which reclaimed acetone was being accumulated. No further processing would be required prior to shipment. The contaminated aqueous residue (reboiler contents) was shipped to another TSDF for further treatment and disposal at a facility which accepts dilute waste.

The results of analyzing the waste material in the reboiler during stripping is presented in Tables 54 and 55. These results are also graphically presented in Figures 36 and 37.

In the acetone batch, the relative rate of removal of all the compounds was to be approximately the same rate, with the xylene and isopropanol being somewhat more slowly removed (Figure 37). There was removal of all the VOCs to less than 700 ppm in the final treated waste, with 99.7 percent removal of acetone.

As the waste material is stripped, the vapor phase concentration of the volatile organic compounds at equilibrium in the cool waste decreases as their concentrations decrease. In Tables 56 and 57, it is apparent that the volatility characteristics of the wastes are dramatically altered by the steam distillation process. These volatility characteristics of the cooled wastes are of concern because of the relation between the vapor pressure of the volatile components and its release into the atmosphere upon disposal. The waste material generally showed at least an order of magnitude decrease in the vapor concentrations at equilibrium with the waste.

In the methyl ethyl ketone (MEK) batch, there were two major components which were removed from the organic waste: 2,2-dimethyl oxirane (DMO) and MEK. MEK and DMO were removed from the process with less than 10 ppm remaining after 615 minutes. The trichloroethane was somewhat more slowly removed with 530 ppm or 0.05 percent residual trichloroethane in the water material after 720 minutes. The methylene chloride was rapidly removed from the batch with greater than 99.7 percent removal after 215 minutes. The data from the 1,1,1-trichloroethane were anomalous and unexplained. The other major components were removed to below the detectability limits of the process.

The distillation of individual components in a dilute aqueous phase is expected to occur independently. That is, the concentration decrease of one component is not expected to be significantly influenced by the composition of

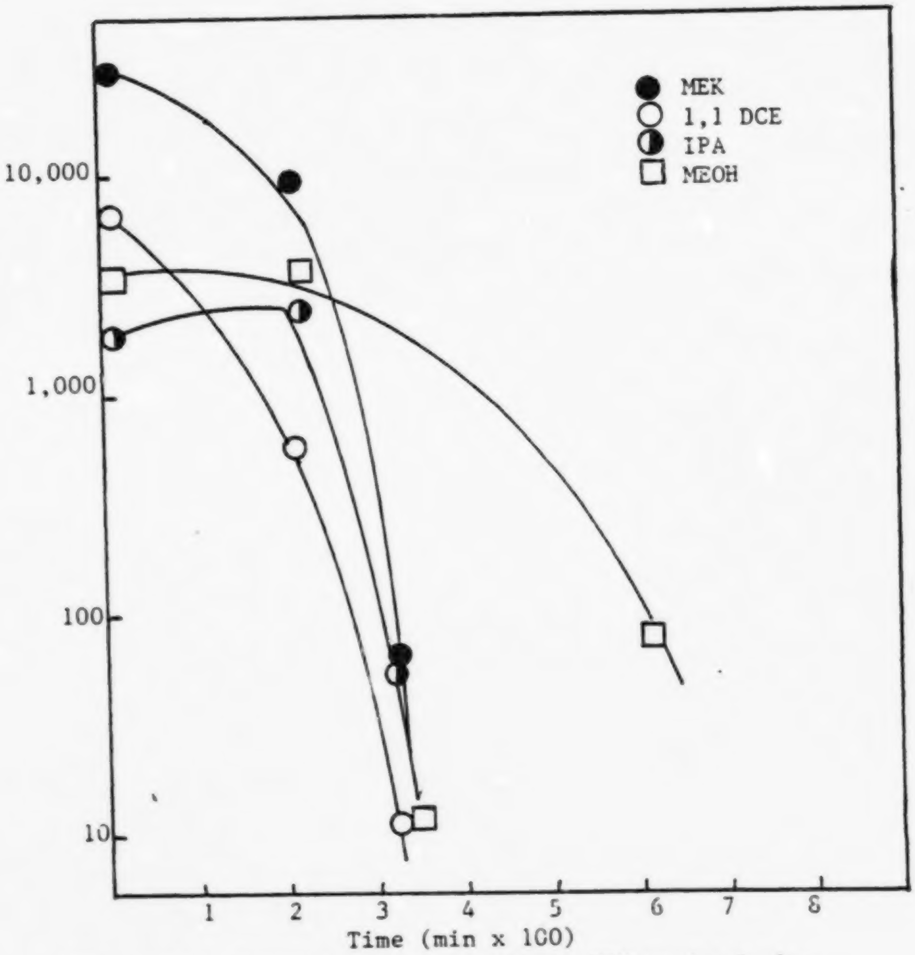


Figure 36. Concentrations of VOC in MEK waste during distillation stripping.

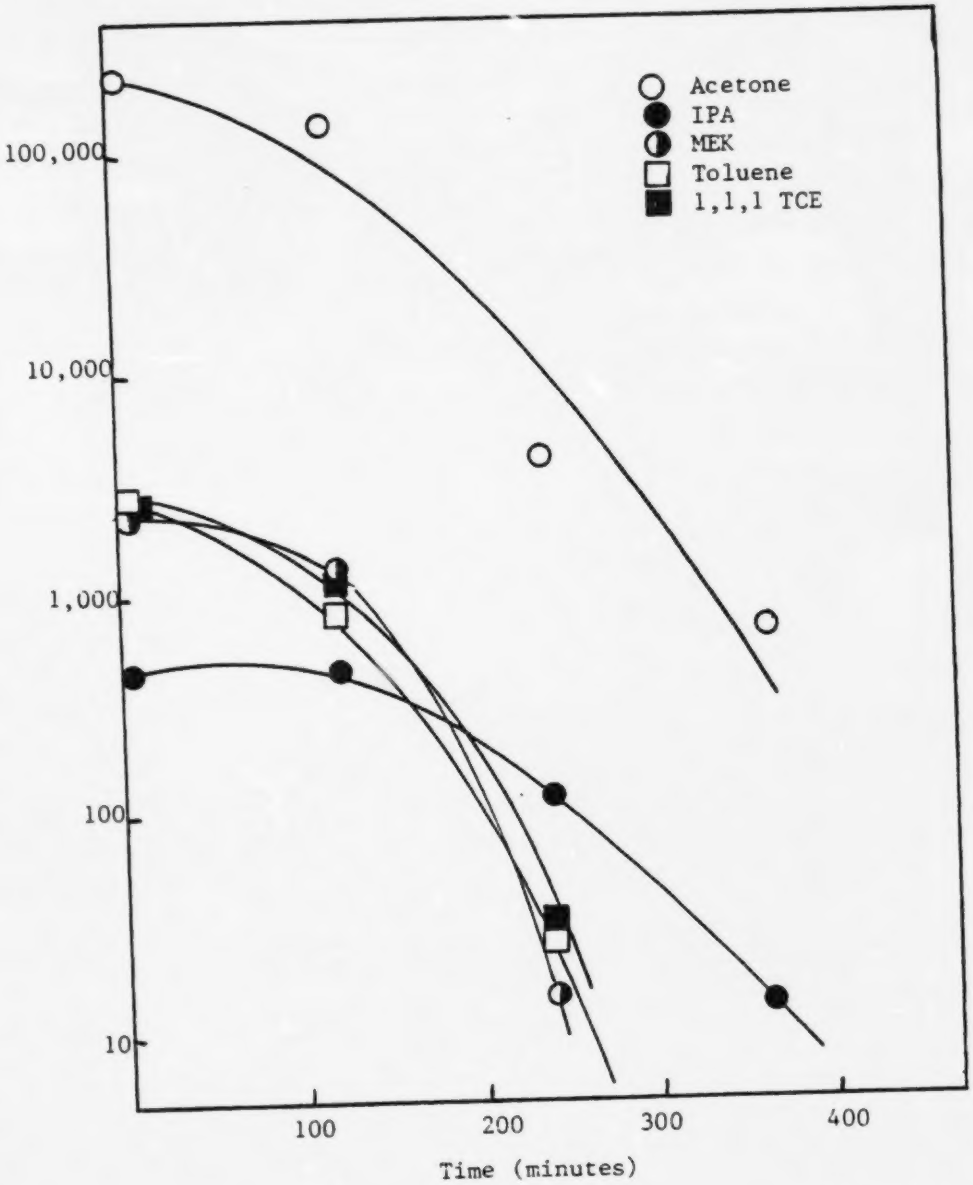


Figure 37. Concentrations of VOC in acetone waste during distillation.

TABLE 54. CONCENTRATIONS OF VOC IN ACETONE BATCH

Sample number	Process time (Minutes)	Trichloro-ethene (mg/L)	Toluene (mg/L)	Ethyl benzene (mg/L)	Xylenes (mg/L)	Acetone (mg/L)	Isopro-panol (mg/L)	Methyl ethyl ketone (mg/L)	1,1,1-Tri-chloroethane (mg/L)
250039	0	9,500	2,700	91	200	212,000	440	2,300	2,800
250041	120	<10	820	41	110	140,000	430	1,300	1,100
250042	240	<10	28	10	<10	4,100	110	14	32
250043	364	<10	<10	<10	<10	690	13	<10	<10

TABLE 55. CONCENTRATIONS OF VOC IN METHYL ETHYL KETONE BATCH

Sample number	Process time (minutes)	MEK (mg/L)	2,2-Dimethyl oxirane (mg/L)	Isopropanol (mg/L)	Methylene chloride (mg/L)	1,2-Dichloroethene (mg/L)	Methanol (mg/L)	1,1,1-Trichloroethane (mg/L)	Trichloroethene (mg/L)	Carbon tetrachloride (mg/L)	Benzene (mg/L)
250030	0	30,000	6,400	1,900	3,100	320	3,500	710	520	1,700	260
250033	215	9,400	490	2,500	<10	310	3,400	550	990	2,200	500
250036	325	61	<10	52	<10	<10	<10	350	350	<10	190
250037	615	<10	<10	<10	<10	<10	75	1,100	110	<10	210
250038	720	<10	<10	<10	<10	<10	<10	530	<10	<10	<10

TABLE 56. CONCENTRATIONS OF VOC IN HEADSPACE OVER BATCH RESIDUE AS A FUNCTION OF STRIPPING TIME. ACETONE BATCH

Sample number	Process time (Minutes)	Acetone (mg/L)	Methyl ethyl ketone (mg/L)	Tetra-chloro-ethene[a] (mg/L)	Toluene (mg/L)	Xylenes (mg/L)	1,1,1-Tri-chloro-ethane (mg/L)
250039	0	340	0.4	1.1	<0.1	1.3	0.67
250041	120	280	0.5	0.32	1.8	2.2	0.21
250042	240	7.1	<0.1	0.39	<0.1	0.37	0.49
250043	364	2.1	<0.1	<0.1	<0.1	0.11	0.22

[a] Concentration in the liquid was below the detectability limit 10 mg/L.

TABLE 57. CONCENTRATION OF VOC IN HEADSPACE OVER BATCH RESIDUE AS A FUNCTION OF STRIPPING TIME. MEK BATCH

Sample number	Process time (Minutes)	Methylene chloride (mg/L)	Methyl ethyl ketone (mg/L)	2,2-Dimethyl-oxirane (mg/L)	Carbon tetra-chloride (mg/L)
250030	0	0.49	91	24	1.7
250033	215	0.21	21	0.37	1.1
250036	325	0.10	<0.10	<0.10	<0.1
250037	615	<0.10	1.12	<0.10	<0.1
250038	720	0.10	<0.10	<0.10	<0.1

the other components. The rate of stripping of dilute compounds is expected to be proportional to the amount of material present. Therefore, the rate decreases as the batch is stripped to completion. One of the characteristics of first-order decay processes is that the logarithm of the concentration is proportional to time plus a constant. The value of the constant is specified so that the concentration equals the initial concentration at the beginning of the stripping process. To verify the first-order decay model, the results from the batches are plotted as logarithm of the concentration versus time in Figures 36 and 37.

For distillation systems in which a layer of organic material is being stripped with an aqueous phase (this was not the case for the two batches tested), the concentration in the aqueous phase may not fall as rapidly initially as later in the process. If there is a layer of organic on water, the organic components present as a liquid would need to be removed by the stripping process (leaving only an aqueous phase) before very low levels of these organic components could be obtained in the aqueous phase through the stripping process. In addition, distillation can provide a relatively clean "cut" of the more volatile components. The less volatile organics may be returned by reflux to the top of the column and ultimately to the reboiler.

For organic waste materials, some of the more volatile components are removed from the reboiler initially. The temperature above the batch being stripped will reflect the equilibrium concentrations of the vapors of these components.

Table 58 presents a summary of the data analysis of the two batches evaluated at Plant B. The correlation coefficient was relatively high for many of the rates of stripping. The steam rate influences the rate of stripping, so the rate constants are presented in a dimensionless form to account for the steam rate and batch size.

The data in Figures 36 and 37 were correlated with a least-squares analysis for the logarithm of the concentration as the independent variable and with the time of distillation as the dependent variable. The negative of this slope of the linear correlation is the stripping rate constant. Figures 36 and 37 are obviously not represented by a straight line, within the limits of the data precision and particularly for the initial part of the removal curve.

Process Residuals

Air Emissions--

In addition to the removal of VOCs from the waste material, the absence of significant treatment process emissions is also of interest. The treatment after disposal would be of little use if substantial quantities of VOCs are released to the atmosphere during processing.

The air emission sources from the two different distillation processes were evaluated at Plant B. The vent locations are indicated in a typical process diagram of the equipment which is presented in Figure 35. In both columns, the condenser was vented to the atmosphere on the downstream side of

TABLE 58. SUMMARY OF DISTILLATION VOC REMOVAL RATES

Batch	Component	Correlation coefficient	Stripping rate constants		
			Minutes^{-1}	90% Limits	Dimensionless[a]
Acetone	acetone	0.963	0.017	0.0097	18.9
Acetone	isopropanol	0.931	0.00986	0.0796	10.9
Acetone	methyl ethyl ketone	0.927	0.0171	0.00141	19.0
Acetone	1,1,1-Trichlorethane	0.971	0.0168	0.0086	18.6
Acetone	toluene	0.975	0.0166	0.0079	18.5
Acetone	xylene	0.931	0.0094	0.0076	10.4
MEK[b]	methyl ethyl ketone	0.874	0.0172	0.0635	36.0
MEK	isopropanol	0.923	0.00947	0.0099	19.8
MEK	methanol	0.763	0.00766	0.0088	16.0
MEK	benzene	0.708	0.00366	0.00469	7.6
MEK	trichloroethene	0.856	0.00526	0.00432	11.0
MEK	2,2-dimethyl oxirane	0.967	0.0188	0.0368	39.4

[a] Obtained by multiplying the stripping constant by the ratio of the batch size to the steam rate.

[b] The correlation coefficients are relatively low for the MEK batch because of the nonlinearity of the data.

the product flow through a vertical atmospheric vent with a tee near the top and a vertical pipe with a discharge several meters lower than the tee. The upper condenser discharge was beneath metal plates in the scaffolding support. The condenser vent on the 110 cm (42-inch) column was accessible for air sampling and velocity determinations as planned, but the vent on the condenser from the 81-cm (32-inch) column was inaccessible for the measurement of velocities due to personnel safety consideration. Air sampling was obtained on the condenser vent and the receiver vent of the 81-cm (32-inch) column at approximately mid-cycle. With a cross-sectional area of 13 cm^2 (0.014 ft^2), the average flow during a 10-minute period was estimated to be less than 1.3 L/sec (0.05 ft^3/sec).

The product vent of the MEK batch was sampled during filling, and visible fumes were observed with a relatively low velocity. The volumetric flow rate from the product vent was assumed to be equal to the volume displaced by the product. The temperature in the gas vent was measured with a mercury thermometer where accessible. The temperature of gas emitted from the condenser vent on the 110-cm (42-inch) column was typically slightly warmer than the atmosphere, indicating that some of the flow from the vent could have originated with the distillation process.

The air emissions were estimated on both batches. The results of the concentrations obtained from air samples taken from the vents are presented in Tables 59 and 60. In addition to the concentrations in the air samples, some of the equilibrium vapor analyses obtained on liquid samples are presented in Tables 59 and 60 for comparison. The concentrations of the equilibrium over the distillate obtained midway through the process correlated within a factor of 33 percent with the concentrations obtained from the material in the vapor phase of the MEK process. The concentrations in the air emission decreased as the batch was processed, and the concentrations in both the laboratory analysis of headspace over the distillate and the reboiler contents tended to decrease as the batch was processed. The average emissions are expected to be a combination of both the rate of flow and the composition drift of the various components. Table 61 estimates the air emissions on the basis of the average of the results of the tests on three air samples taken from the aqueous MEK batch. The estimates of air emissions from the acetone batch is presented in Table 62. The volumes emitted from the vents were estimated on the basis of the data obtained from waking losses and vent velocity measurements. The same procedure was used with the acetone batch and presented in Table 62. In both cases, the emissions were only a small fraction of the VOCs recovered from the process.

Process Cost

A listing of waste treatment costs provided by Plant B is presented in Section 7, Page 77.

TABLE 59. AIR SAMPLES: METHYL ETHYL KETONE WASTE PROCESS

Sample number		Time	Methyl ethyl ketone (mg/L)	Acetone (mg/L)	2,2-Dimethyl oxirane (mg/L)	Carbon tetrachloride (mg/L)	Methyl alcohol (mg/L
202	Field ambient		<0.10	<0.10	<0.10	<0.10	<0.10
201	Condenser vent	10:42A	190	55.3	488	15	14.3
31	Distillate[a]	11:25A	130	47	330	<0.1	11
206	Condenser vent	1:14P	0.27	0.10	0.12	<0.1	<0.1
205	Condenser vent	1:19P	0.12	<0.1	<0.1	<0.1	<0.1
34	Distillate[a]	1:20P	200	7.2	41	<0.1	6
204	Condenser vent	2:49P	6.5	0.16	0.49	<0.1	0.98
203	Accumulator vent	2:05P	1.2	0.80	4.9	0.16	<0.1
35	Distillate[a]	2:25P	140	2.1	10	1.4	6.2

[a] Laboratory analysis of vapors in headspacing above distillate. Vent samples reported above the distillate headspace analysis were taken at approximately the same time as the distillate.

TABLE 60. AIR SAMPLES: ACETONE WASTE PROCESS

Sample number		Time	Acetone (mg/L)	Methyl ethyl ketone (mg/L)	Chloroform (mg/L)	Isopropyl alcohol (mg/L)	Methylene chloride (mg/L)
202	Field ambient		<0.1	<0.1	<0.1	<0.1	<0.1
207	Condenser vent	10:31A	1.1	<0.1	<0.1	<0.1	<0.1
208	Receiver vent	10:42A	1.5	<0.1	<0.1	<0.1	<0.1
209	Product vent	11:39A	1.7	452	<.1	34	5.7
40	Distillate	11:00A	490	<0.1	1.9	<0.1	<0.1
210	Condenser vent	2:36P	1.3	<0.1	0.14	<0.1	<0.1
212	Condenser vent	2:37P	0.98	<0.1	0.21	<0.1	<0.1
44	Composite distillate	10:00A 3:30P	450	0.21	1.2	<0.1	<0.1

TABLE 61. AIR EMISSIONS: METHYL ETHYL KETONE PROCESS

Source	Time	VOC (mg/L)	Flow (L/s)	Emissions (g/s)
Condenser vent 1	10:42A	762	0.72	0.55
Condenser vent 2	1:15P	0.26	0.41	0.00011
Condenser vent 3	2:50P	8.1	0.8	0.0064
Condenser vent average				0.186
Accumulator vent	2:05P	7.1	0.4[a]	0.0028[a]

[a] Maximum from working losses: not representative of process

TABLE 62. AIR EMISSIONS: ACETONE PROCESS

Source	Time	VOC (mg/L)	Flow (L/s)	Emissions (g/s)
Condenser vent 1	10:31A	1.1	<1.3	<0.0014
Condenser vent 2	2:36P	1.3	<1.3	<0.0017
Condenser vent average				<0.0016
Receiver vent	10:42A	1.5	<0.6[a]	<0.0009[a]
Receiver vent	10:42A	1.5	1.0[b]	0.0015

[a] Estimated as less than half of the flow from the condenser vent.
[b] Estimated from average product reflux rate.

DISTILLATION FIELD EVALUATION AT PLANT E

Process Description

Plant E is primarily engaged in reclamation and recycle of waste organic solvents and contaminated products. The processes utilized at the Plant E facility are distillation which includes fractionation and thin-film evaporation. These are technologies which are of interest for removal of VOC from waste streams.

Plant E is situated on about 7 acres of land, with the primary activity being the reclamation and recycle of waste solvents and contaminated products. Reclaimed solvents which are not recycled back to the generator are marketed to suitable end uses. Special blends may be produced for these sales. Approximately 23 million liters (6 million gallons) per year of solvent is recovered.

The recovery and purification processes involve four distillation systems:

One Votator thin-film evaporator,

One continuous fractionation distillation,

Two batch fractionation distillations.

Support facilities include a hot oil process heat system, a cooling water system, and a building providing housing for offices and a laboratory. A fleet of tank trucks is maintained for transport of all incoming and outgoing bulk shipments.

Waste organic solvents and contaminated products are received in bulk and drum shipments and are processed for reclamation and recycle. Each shipment of chemicals received is analyzed to verify the manifest identification.

The contaminated solvent is processed through one of the four distillation systems, with the reclaimed product being taken off overhead. The system selected is dependent upon the characteristics of the particular stream being processed, and in some cases additional purification may be required.

Process Effectiveness

The process effectiveness of the distillation process was not evaluated during the 1-day visit.

Process Residuals

Distillation bottoms are disposed of in one of several ways with the most attractive option being utilization in fuel in cement kilns. In order to be acceptable as fuel, a minimum heat value must be maintained, resulting in the loss of some solvent, and the halogen content must not be greater than 4 percent. Still bottoms which are unacceptable as fuel are solidified and landfilled. In the case of dilute aqueous streams (less than 2 percent organics), disposal is through offsite land treatment.

Process Cost

The following data were obtained from Plant E personnel:

1. The cost of simple distillation is in the range of \$0.21 per liter (\$0.80 per gal) of solvent recovered.

2. Reclamation cost could be as high as \$0.70 per liter (\$3 per gal) if multiple distillations were required to achieve the desired level of purity.

3. It is not economical to reduce VOCs in aqueous streams below 2 percent by fractionation at Plant E. The cost could be as high as \$1.50 per liter (\$6 per gal)

4. Aqueous waste containing less than 2 percent organics can be land-treated at a cost of about \$0.11 per liter (\$0.40 per gal). This includes \$0.022 per liter (\$0.08 per gal) transportation cost.

5. It was estimated that the cost to ship waste to Houston (approximately 1,500 miles) and incinerate would be in the range of \$0.79 per liter (\$3 per gal).

6. The cost of landfilling including transport, superfund tax, State tax, and landfill fee is now \$0.30 per liter (\$1.06 per gal) for hazardous waste and \$0.33 per liter (\$1.20 per gal) for waste which the State defines as "restricted." The above prices are only applicable if the material is already solid. The average price of waste disposal is \$0.60 per liter (\$2.18 per gal), including solidification.

SECTION 10

SUMMARY

This section summarizes the differences among the various treatment techniques and identifies similarities of applicability.

APPLICABILITY OF WASTE TREATMENT

Of primary concern in assessing the applicability of a technique for VOC removal is the answer to the question, "Can it be used to treat the waste?"

Liquids

Liquids are classified for pretreatment purposes into aqueous wastes, mixed organic and aqueous wastes, and organic wastes. Other waste characteristics include dissolved solids, suspended solids, and viscosity. A thin-film evaporator can treat each of these waste categories, as long as the viscosity is not greater than 10,000 cp. Some additional processing may be needed for the condensed aqueous vapors from the evaporators, which generally will contain volatiles.

Steam strippers can treat nonviscous liquids, with a limited ability to process wastes with dissolved and suspended solids.

Distillation can be used to treat nonviscous liquids with restricted abilities to process dissolved and suspended solids because of potential reboiler heat exhange surface and column plate fouling.

Reactive Wastes

Reactive wastes such as free-radical polymerization monomers must be stabilized before processing with the thin-film evaporator. Problems can occur (Plant A, Plant B) when these materials are processed. Polymerization in the reboiler of a distillation column is dangerous. A steam stripper can be successfully used to process some of these reactive wastes because of the lower temperature of the steam (Plant D).

Sludges

Thin-film evaporators can be used to process sludges (viscosity less than 100 poise). The amount of material recovered depends on the properties of the bottoms. Sludges generally are not processed in the steam stripping unit at Plant D and in the distillation units at Plant B.

Solids

Unless the solids become liquids when heated, solids are not appropriate for processing in thin-film evaporators, steam stripping units, or distillation units. Some problems can occur for the recovery of organics which solidify upon condensing the vapors. Scraping condensers or upflow condensers are options for resolving condensing solids problems.

EFFECTIVENESS OF WASTE TREATMENT

The effectiveness of thin-film evaporators, steam strippers, and distillation to remove VOCs are compared. Table 63 presents a summary of the percent VOC removal obtained for the processes and wastes investigated.

Liquids

Thin film evaporators are mainly used to remove VOCs by volume reduction. In the processing of high boiling point chlorinated xylenes (Plant A), the removal of VOCs was very high (>95 percent) but the removal of the chlorinated xylenes was also high. When the liquid was primarily VOCs (Plant B and Plant C), the bottoms still contained a high fraction of VOCs, but the volume was reduced.

In the cases of steam stripping and distillation, the removal of VOCs from the waste is characteristically high (>99 percent), and the VOCs can be removed to achieve even lower concentrations in the residual waste by extending the process time. The oil can be separated from the volatiles by distillation and steam stripping.

Reactive Waste

Reactive waste treatment was not investigated, but the removal effectiveness is expected to be comparable to the liquids (if the waste can be processed).

Sludges

The treatment of sludges was not investigated in thin-film evaporators, but the removal effectiveness of VOCs from the waste is expected to be limited (only 1-1.5 theoretical trays) unless the sludge is recycled.

Solids

The effectiveness of treating solids was not investigated.

COST OF WASTE TREATMENT AND RESIDUALS DISPOSAL

Table 64 presents general unit costs for waste treatment that were obtained from the facilities during this study and which have have been presented on a plant-by-plant basis in Sections 7-9. These are typical facility costs, representing approximate 1984 annual averages as estimated by the operators.

TABLE 63. EFFECTIVENESS OF WASTE TREATMENT

Process	Plant	Waste	Compound	Percent removal
Thin film evaporator	A	Oil	Toluene	95
Thin film evaporator	A	Oil	Chloroform	>99
Thin film evaporator	A	Oil	Methylene chloride	>99.91
Thin film evaporator	B	VOC	Isopropyl alcohol	-113[a]
Thin film evaporator	B	VOC	Freon TF	86[a]
Thin film evaporator	B	VOC	Xylenes	-77[a]
Thin film evaporator	C	VOC resin	Acetone	78
Thin film evaporator	C	VOC resin	Xylene	23
Steam stripping	C	Aromatic in water	VOC	99.8
Steam stripping	C	VOC in oil	VOC	99.8
Steam stripping	C	Chlorinated in H_2O	VOC	93
Steam stripping	C	VOC in water	VOC	99
Distillation	B	MEK in water	VOC	99
Distillation	B	Acetone in water	VOC	99.8

[a] Percent reduction in vapor pressure of headspace.

TABLE 64. 1984 UNIT COSTS PROVIDED BY PLANT PERSONNEL

Liquid disposal, landfarm	\$0.11[a]
Liquid disposal, landfill	\$0.60[a]
Bottoms disposal, landfill	\$0.30[a]
Bottoms disposal, landfill	\$0.36/L + freight[b]
Bottoms disposal, fuel	\$0.079-\$0.13/L + freight and drumming
Bottoms disposal, fuel	\$0.05/L[c]
Bottoms disposal, incinerate[g]	\$0.79/L[a]
Bottoms disposal, shipping, fuel	\$0.05-\$0.08/L[d]
Aqueous bottoms disposal, wastewater treatment	\$0.00005/L[e]
Operating cost organic overhead	\$0.26/L VOC[b]
Operating cost organic overhead	\$0.26/L VOC[d]
Operating cost organic as bottoms	\$0.40/L VOC[d]
Operating cost organic overhead	\$0.057-\$0.33/L VOC[f]
Operating cost multiple distillation	\$0.70/L VOC[a]
Operating cost simple distillation	\$0.20/L VOC[a]
Limit of economical VOC recovery	6-8 percent[d]
Limit of economical VOC recovery	2 percent[a]

[a] Plant E distillation.

[b] Plant C thin-film evaporator.

[c] Plant A thin-film evaporator.

[d] Plant B thin-film evaporator.

[e] RTI estimate, presented for comparison.

[f] Plant D direct steam stripper.

[g] Includes cost of transporting waste 1,500 miles.

Table 65 summarizes waste-stream specific unit costs that were calculated in the present investigation. Both operating and equipment costs are included in the annualized costs in this table. Modelled (i.e., hypoethetical treatment) cost estimates are given for thin-film evaporation and distillation. In the case of steam stripping and one thin-film evaporator facility (Plant A), sufficient data were available from the facility to estimate unit operating costs for actual waste streams and equipment combinations. Comparison of the unit costs calculated in Table 65 shows that treatment costs vary as a function of treatment technique, initial VOC content, and process load (volume/minute).

Thin-Film Evaporation

Thin-film evaporators typically have a unit operating cost of approximately \$0.26/L VOC recovered overhead (both Plants B and C). These costs are sensitive to both the concentration of VOCs and the volume of waste treated. The costs can increase to \$0.30/L VOC recovered (excluding equipment costs) for a waste with 2-percent VOC or decrease to a low of \$0.033/L VOC recovered for greater than 50-percent VOC recovery.

Steam Stripping

A range of product recovery costs for the steam stripping system at Plant D was estimated by plant personnel to typically be \$0.057-\$0.33/L VOC recovered. This range is approximately the same as for the thin-film evaporator. However, one of the three waste streams that were being processed by the plant at the time of the field assessment was estimated to have a treatment cost of \$0.83/L, while the fourth (synthetic) stream, which has a VOC concentration lower than the plant typically processes, was estimated to cost \$4.34/L VOC removed.

Distillation

The costs of distillation are estimated by Plant E to range from \$0.20/L of recovered VOC for simple distillation to \$0.70/L of recovered VOC for multiple distillation. The cost of simple distillation is within the same range as that estimated for thin-film evaporators and steam stripping. However, the cost for VOC removal from a hypothetical stream having low initial VOC content (3 percent) was estimated to be \$1.81/L (Table 65), indicating that distillation costs may increase significantly as the initial VOC content of the waste decreases.

Economical Recovery of VOCs

A TSDF can treat the waste and recover the VOCs, or the TSDF can dispose of the waste. Table 66 presents the results of an analysis of the cost of treating various concentrations of VOC in the waste streams with the same characteristics as Batch 1 at Plant D. The cost of treating the waste increases with decreasing VOC content because of the low recovered VOC credits possible at low initial concentrations and because the VOC removal rate is proportional to the VOC content of the waste.

TABLE 65. 1984 UNIT COSTS[a] OBTAINED FROM THE CURRENT INVESTIGATION

	Thin film evaporator		Distillation	Steam stripping (Plant D)[e]			
	Modelled[b]	Plant A[c]	Modelled	Batch 1	Batch 2	Batch 3	Batch 4
Annualized cost	157.5	252.6	359.2	262.9	262.9	262.9	262.9
Flow rate (L/M)	40	32	260	8	6	5	5
VOC content (percent)	2	85	3	26	74	18	3
Unit Costs							
$/L Waste treated	0.0075	0.0279	0.035	0.08	0.12	0.15	0.16
$/L VOC recovered	0.37	0.033	1.18	0.30	0.17	0.53	4.34
$/Mg VOC (Density = 0.8)	462	41.1	1,475	376	210	659	5,358

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[a] Includes waste-stream specific operating costs and annualized equipment costs.

[b] Source: Table 15

[c] Source: Table 20

[d] Source: Section 6, COST

[e] Source: Tables 28 and 46

TABLE 66. THE COSTS OF STEAM STRIPPING AS A FUNCTION OF THE VOC CONTENT OF THE WASTE

Fraction VOC content	Product credit[a]	$ recovery/L[b]
0.35	203,260	0.020
0.26	151,000	0.039
0.10	58,000	0.071
0.05	290,000	0.081
0.01	5,800	0.089

[a] Based on a waste volume of 2,904,000 L/year, $0.20/L VOC product recovery credit, 99.7 percent recovery.

[b] Based on an operating cost of $262,900/year.

TABLE 67. A COMPARISON OF TREATMENT VERSUS DISPOSAL COSTS FOR 200 L (55 GALLONS) OF AQUEOUS WASTE CONTAINING 2-5% VOC

Treatment Costs	
Treat Stream of 2% VOC by thin-film evaporation[a]	$2
Treat Stream of 3% VOC by distillation[a]	$7
Treat Stream of 3% VOC by steam stripping[a]	$37
Treat Stream of 5% VOC by steam stripping[b]	$16
Disposal Costs	
Land Treatment	$22
Landfill	$120
Incinerate	$158

[a] Basis: Table 65

[b] Basis: Table 66

[c] Basis: Table 64, Plant E.

Waste treatment costs are compared to selected waste disposal costs in Table 67. Treatment costs for aqueous waste containing 2-5 percent VOC are presented, based on Tables 65 and 66. Costs are compared for treating or disposing of 200 L (55 gallons) of waste, typical of a disposal decision faced by many generators. It is assumed that once the waste has been treated to remove VOCs, the waste is no longer hazardous, i.e., the cost of disposal of the treated waste is negligibly small. This a good assumption, for instance, if the treated aqueous effluent is acceptable for discharge to a municipal sewer. Based upon this analysis, the cost of steam stripping is less than disposal costs by landfilling and incineration, but competitive with land treatment.

The various plants suggested that a limit of economic viability exists for wastes with low VOC contents. These limits range from 2 percent at Plant F to 6-8 percent at Plant B. The range of costs for economic viability suggests that either the disposal costs are overestimated or the waste treatment facilities are utilized at a level which is substantially under capacity. If the TSDF has an onsite disposal method for dilute VOC treatment, the disposal costs could be substantially less than commercial rates.

MEASURED AIR EMISSIONS

Air emissions were measured at several of the TSDF processes which were investigated. The results are presented in Tables 68 and 69.

Thin-Film Evaporators

Of the three thin-film evaporators evaluated, two were operating under vacuum (Plants A and B) and one was operating under atmospheric pressure (Plant C). Visible emissions were observed from the vacuum vent (connected to the process). The data from the vacuum pumps are not supported with measured volumetric flow rates, but relatively high concentrations of VOCs were associated with the vacuum pump vent. In contrast, the concentration and flow rate from the atmospheric thin-film evaporator process were negligible during the process assessment at Plant C. The emission factor (g/g VOC recovered) was estimated to be relatively low (less than 2 percent) for the thin-film evaporators operating under vacuum, but substantially greater than the vents from the steam stripping and distillation processes.

Steam Stripping

The condenser on the steam stripping unit at Plant D was vented onto the roof. The emissions were greater at the beginning of the process and decreased toward the end of the run as the concentrations of the VOCs in the batch were reduced. The emissions were 0.0029 g/sec for the first batch and 0.0035 g/sec for the second batch. The emission factors were 5.7×10^{-5} and 2.7×10^{-5} g/g VOC, respectively, for these two batches. This represents only a small fraction of the VOCs recovered.

TABLE 68. CONDENSER VENT EMISSIONS

Location	Source	Rate (g/sec)	Emission factor (g/g VOC)
Plant D	Condenser vent, Batch 1	0.0029	5.7×10^{-5}
Plant D	Condenser vent, Batch 2	0.0035	2.7×10^{-5}
Plant B	Condenser vent, MEK[a]	0.186	6.0×10^{-4}
Plant B	Condenser vent, Acetone[b]	<0.0016	9.8×10^{-7}
Plant A	Condenser vent, TFE[c]	-	0.026
Plant B	Condenser vent, TFE	-	-
Plant C	Condenser vent, TFE[d]	-	No measurable emissions

[a] Batch size = 30,280 L x .044 Kg/L; 1,332 kg, 4,320 sec.

[b] Batch size = 11,335 L x .227 Kg/L = 3,573 kg, 2,184 sec.

[c] 0.02 x .57 + 0.015 x .99 = 0.026, vacuum process.

[d] Nonvacuum process.

TABLE 69. STORAGE TANK EMISSIONS

Location	Source	Rate
Plant C	Outside storage tank	.63 g/sec
Plant D	Inside vented storage tank	0.0004 g/sec
Plant D	Inside vented MST	0.0024 g/sec
Plant B	Accumulator tank	0.0028 g/sec
Plant B	Receiver vent	0.0015 g/sec

Distillation

Although the process condenser vent for the distillation of the first batch at Plant B had a much higher emission rate than the condenser vent at Plant D (0.186 g/sec) by a factor of 60, the emission factor (0.0006 g/g VOC) was only a factor of 10 greater. The estimated emissions for the second batch was comparable to the emissions from Plant D (factor of 2 lower), but due to the greater batch volume at Plant B, the emissions factor was much lower (factor of 100). The distillation vent emissions were much less than the recovered VOCs.

Storage Tanks

The air emissions estimates for product and waste storage tanks are presented in Table 69. In general, the emissions are relatively low compared to the amount of waste processed. The open storage tank at Plant C had substantially greater emissions (0.63 g/sec) than comparable enclosed storage tanks (by a factor of 250), suggesting that enclosing and venting the tanks can reduce emissions by greater than 99 percent.

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APPENDIX A

SUMMARY OF ANALYTICAL DATA

Table A-1 presents the name of the plant in the first column, followed by the location of the sample in the process, and then followed by either the batch or process from which the sample was taken. The concentration in the aqueous phase of the sample (or the concentration in the organic phase if the sample is mainly organic) is presented in the fourth column, followed by the calculated value of Henry's constant for the sample and the concentration in the vapor phase. The partition coefficient (mole fraction, Y, in the vapor divided by the mole fraction, X, in the liquid) is presented in the seventh column. The Henry's constant is not defined by the partition coefficient for complex waste mixtures, as it is for dilute aqueous mixtures. The calculated values of the mole fraction of the VOCs in the liquid and vapor are presented in the last two columns.

The following abbreviations are used:

REB - reboiler contents
DISTIL - distillate
MST - miscible solvents tank
STRIP. - stripper contents
CONDEN - condensate
TFE - Thin-film evaporator

The units of Henry's constants are atm-m^3/mole, A - m^{3}m. The Henry's constants have been multiplied by 1,000 for presentation in this table. Note that this is a computer listing and therefore more significant figures are sometimes shown than are warranted by the precision of the results. Refer to the text for the correct number of significant figures.

TABLE A-1. ANALYSIS OF LIQUID WASTE SAMPLES

PLANT	SAMPLE NUMBER	LOC.	BATCH OR PROCESS	COMPONENT	LIQUID CONC. (mg/L)	H CONST. A/M*M3 *E-3	VAPOR CONC. (mg/L)	K (Y/X)	MOLECULAR WEIGHT	X	Y
PLANT B	25.30	REB 1	1	METHANOL	3500	0.00493	0.84	0.263	32	0.002040	0.000538
PLANT B	25.30	REB 1	1	METHYLENE CHLORIDE	3100	0.00324	0.49	0.173	85	0.000680	0.000118
PLANT B	25.30	REB 1	1	ACETONE	0		3.00		58	0	0.001061
PLANT B	25.30	REB 1	1	ISOPROPANOL	1900	0.00994	0.92	0.532	60	0.000590	0.000314
PLANT B	25.30	REB 1	1	DIMETHYL OXIRANE 2,2	6400	0.07696	24.00	4.124	99	0.001206	0.004974
PLANT B	25.30	REB 1	1	METHYL ETHYL KETONE	30000	0.06225	91.00	3.336	72.1	0.007762	0.025901
PLANT B	25.30	REB 1	1	TRICHLOROETHANE 1,1,1	710	0.01156	0.40	0.619	133	0.000099	0.000061
PLANT B	25.30	REB 1	1	CARBON TETRACHLORIDE	1700	0.02052	1.70	1.099	153.8	0.000206	0.000226
PLANT B	25.30	REB 1	1	TOLUENE	18	0.27362	0.24	14.66	92.1	0.000003	0.000053
PLANT B	25.30	REB 1	1	XYLENES	0		0.23		106	0	0.000044
PLANT B	25.30	REB 1	1	WATER	95.27%	540.90	25.11	0.028	18	0.987410	0.028627
PLANT B	25.30	REB 1	1	TOTAL ORGANICS	47328						
PLANT B	25.31	DISTIL.	1	METHANOL	40000	0.00564	11.00	0.133	32	0.052980	0.007054
PLANT B	25.31	DISTIL.	1	METHYLENE CHLORIDE	2000	0.01744	1.70	0.411	85	0.000997	0.000410
PLANT B	25.31	DISTIL.	1	ACETONE	71000	0.01358	47.00	0.320	58	0.051884	0.016629
PLANT B	25.31	DISTIL.	1	ISOPROPANOL	1000	0.00431	0.21	0.101	60	0.000706	0.000071
PLANT B	25.31	DISTIL.	1	BROMODICHLOROMETHANE	10	5.13046	2.50	121.0	164	0.000002	0.000312
PLANT B	25.31	DISTIL.	1	METHYL ETHYL KETONE	440000	0.00606	130.00	0.143	72.1	0.258658	0.037001
PLANT B	25.31	DISTIL.	1	TRICHLOROETHANE 1,1,1	5000	0.01642	4.00	0.387	133	0.001593	0.000617
PLANT B	25.31	DISTIL.	1	TRICHLOROETHENE	300	0.05609	0.82	1.323	153.8	0.000082	0.000109
PLANT B	25.31	DISTIL.	1	CHLOROFORM	10	2.05218	1.00	48.41	119.4	0.000003	0.000171
PLANT B	25.31	DISTIL.	1	DIMETHYL OXIRANE 2,2	210000	0.03225	330.00	0.760	99	0.089906	0.068406
PLANT B	25.31	DISTIL.	1	WATER	23.07%	2233.84	25.11	0.052	18	0.543183	0.028627
PLANT B	25.31	DISTIL.	1	TOTAL ORGANICS	769320						
PLANT B	25.33	REB 2	1	METHANOL	3400	0.01086	1.80	0.595	32	0.001938	0.001154
PLANT B	25.33	REB 2	1	METHYLENE CHLORIDE	0		0.21		85	0	0.000050
PLANT B	25.33	REB 2	1	ACETONE	100	0.03078	0.15	1.687	58	0.000031	0.000053
PLANT B	25.33	REB 2	1	ISOPROPANOL	2500	0.01313	1.60	0.720	60	0.000760	0.000547
PLANT B	25.33	REB 2	1	DIMETHYL OXIRANE 2,2	490	0.01550	0.37	0.849	99	0.000090	0.000076
PLANT B	25.33	REB 2	1	METHYL ETHYL KETONE	9400	0.04585	21.00	2.513	72.1	0.002378	0.005977
PLANT B	25.33	REB 2	1	TRICHLOROETHANE 1,1,1	550	0.03022	0.81	1.656	133	0.000075	0.000124
PLANT B	25.33	REB 2	1	CARBON TETRACHLORIDE	2200	0.01026	1.10	0.562	153.8	0.000260	0.000146
PLANT B	25.33	REB 2	1	TOLUENE	18	0.00000	0.00	0	92.1	0.000003	0
PLANT B	25.33	REB 2	1	XYLENES	0		0.23		106	0	0.000044
PLANT B	25.33	REB 2	1	WATER	98.13%	525.10	25.11	0.028	18	0.994462	0.028627
PLANT B	25.33	REB 2	1	TOTAL ORGANICS	18658						
PLANT B	25.34	DISTIL.	1	METHANOL	42000	0.00293	6.00	0.053	32	0.071646	0.003847
PLANT B	25.34	DISTIL.	1	METHYLENE CHLORIDE	2000	0.00287	0.28	0.052	85	0.001284	0.000067
PLANT B	25.34	DISTIL.	1	ACETONE	13000	0.01137	7.20	0.208	58	0.012235	0.002547
PLANT B	25.34	DISTIL.	1	ISOPROPANOL	45000	0.00064	1.40	0.011	60	0.040940	0.000478
PLANT B	25.34	DISTIL.	1	CHLOROFORM	10	0.90296	0.44	16.54	119.4	0.000004	0.000075
PLANT B	25.34	DISTIL.	1	METHYL ETHYL KETONE	670000	0.00613	200.00	0.112	72.1	0.507264	0.056926

(CONTINUED)

TABLE A-1. (CONTINUED)

PLANT	SAMPLE NUMBER	LOC.	BATCH OR PROCESS	COMPONENT	LIQUID CONC. (mg/L)	H CONST. A/M*M3 *E-3	VAPOR CONC. (mg/L)	K (Y/X)	MOLECULAR WEIGHT	X	Y
PLANT B	25.34	DISTIL.	1	TRICHLOROETHANE 1,1,1	20000	0.00083	0.81	0.015	133	0.008208	0.000124
PLANT B	25.34	DISTIL.	1	BROMODICHLOROMETHANE	10	1.27235	0.62	23.30	164	0.000003	0.000077
PLANT B	25.34	DISTIL.	1	TOLUENE	15000	0.00030	0.22	0.005	92.1	0.008890	0.000049
PLANT B	25.34	DISTIL.	1	DIMETHYL OXIRANE 2,2	95000	0.00886	41.00	0.162	99	0.052382	0.008498
PLANT B	25.34	DISTIL.	1	WATER	9.80%	5259.27	25.11	0.096	18	0.297139	0.028627
PLANT B	25.34	DISTIL.	1	TOTAL ORGANICS	902020						
PLANT B	25.36	REB 3	1	METHANOL	0		0.20		32	0	0.000128
PLANT B	25.36	REB 3	1	METHYLENE CHLORIDE	0		0.10		85	0	0.000024
PLANT B	25.36	REB 3	1	ACETONE	0		0.00		58	0	0
PLANT B	25.36	REB 3	1	ISOPROPANOL	52	0.00000	0.00	0	60	0.000015	0
PLANT B	25.36	REB 3	1	DIMETHYL OXIRANE 2,2	0		0.00		99	0	0
PLANT B	25.36	REB 3	1	METHYL ETHYL KETONE	61	0.00000	0.00	0	72.1	0.000015	0
PLANT B	25.36	REB 3	1	TRICHLOROETHANE 1,1,1	350	0.01466	0.25	0.814	133	0.000047	0.000038
PLANT B	25.36	REB 3	1	CARBON TETRACHLORIDE	0		0.00		153.8	0	0
PLANT B	25.36	REB 3	1	TOLUENE	22	0.00000	0.00	0	92.1	0.000004	0
PLANT B	25.36	REB 3	1	XYLENES	0		0.00		106	0	0
PLANT B	25.36	REB 3	1	WATER	99.95%	515.55	25.11	0.028	18	0.999917	0.028627
PLANT B	25.36	REB 3	1	TOTAL ORGANICS	485						
PLANT B	25.37	REB 4	1	METHANOL	65	0.00000		0	32	0.000036	0
PLANT B	25.37	REB 4	1	METHYL ETHYL KETONE	10	0.24626	0.12	13.66	72.1	0.000002	0.000034
PLANT B	25.37	REB 4	1	TRICHLOROETHANE 1,1,1	1100	0.00000		0	133	0.000149	0
PLANT B	25.37	REB 4	1	CARBON TETRACHLORIDE	110	0.00000		0	153.8	0.000012	0
PLANT B	25.37	REB 4	1	TOLUENE	17	0.00000		0	92.1	0.000003	0
PLANT B	25.37	REB 4	1	BENZENE	210	0.00000		0	78	0.000048	0
PLANT B	25.37	REB 4	1	WATER	99.85%	516.08	25.11	0.028	18	0.999747	0.028627
PLANT B	25.37	REB 4	1	TOTAL ORGANICS	1512						
PLANT B	25.39	REB 1	2	ACETONE	212000	0.03291	340.00	1.530	58	0.078603	0.120300
PLANT B	25.39	REB 1	2	ISOPROPANOL	440	0.00000		0	60	0.000157	0
PLANT B	25.39	REB 1	2	ETHYLBENZENE	91	0.10374	0.46	4.823	99	0.000019	0.000095
PLANT B	25.39	REB 1	2	METHYL ETHYL KETONE	2300	0.00357	0.40	0.165	72.1	0.000686	0.000113
PLANT B	25.39	REB 1	2	TRICHLOROETHANE 1,1,1	2800	0.00491	0.67	0.228	133	0.000452	0.000103
PLANT B	25.39	REB 1	2	TRICHLOROETHENE	9500	0.00000		0	153.8	0.001328	0
PLANT B	25.39	REB 1	2	TOLUENE	2700	0.00000		0	92.1	0.000630	0
PLANT B	25.39	REB 1	2	XYLENES	200	0.13339	1.30	6.202	106	0.000040	0.000251
PLANT B	25.39	REB 1	2	WATER	76.85%	670.57	25.11	0.031	18	0.918080	0.028627
PLANT B	25.39	REB 1	2	TOTAL ORGANICS	230031						
PLANT B	25.40	DISTIL.	2	CARBON TETRACHLORIDE	10	2.46262	1.20	44.71	153.8	0.000003	0.000160
PLANT B	25.40	DISTIL.	2	BROMOCHLOROMETHANE	10	1.19027	0.58	21.61	129.5	0.000004	0.000091
PLANT B	25.40	DISTIL.	2	ACETONE	850000	0.01183	490.00	0.214	58	0.807110	0.173374
PLANT B	25.40	DISTIL.	2	CHLOROFORM	10	3.89915	1.90	70.79	119.4	0.000004	0.000326
PLANT B	25.40	DISTIL.	2	BROMODICHLOROMETNANE	8000	0.00282	1.10	0.051	164	0.002686	0.000137
PLANT B	25.40	DISTIL.	2	TRICHLOROETHANE 1,1,1	28000	0.00110	1.50	0.019	133	0.011594	0.000231
PLANT B	25.40	DISTIL.	2	TRICHLOROETHENE	42000	0.00018	0.37	0.003	153.8	0.015039	0.000049

(CONTINUED)

TABLE A-1. (CONTINUED)

PLANT	SAMPLE NUMBER	LOC.	BATCH OR PROCESS	COMPONENT	LIQUID CONC. (mg/L)	H CONST. A/M*M3 *E-3	VAPOR CONC. (mg/L)	K (Y/X)	MOLECULAR WEIGHT	X	Y
PLANT B	25.40	DISTIL.	2	TOLUENE	23000	0.00000	0.00	0	92.1	0.013753	0
PLANT B	25.40	DISTIL.	2	TETRACHLOROETHENE	10	1.51862	0.74	27.57	165	0.000003	0.000092
PLANT B	25.40	DISTIL.	2	WATER	4.90%	10524.98	25.11	0.191	18	0.149799	0.028627
PLANT B	25.40	DISTIL.	2	TOTAL ORGANICS	951040						
PLANT B	25.41	REB 2	2	ISOPROPANOL	430	0.00000		0	60	0.000143	0
PLANT B	25.41	REB 2	2	CHLOROFORM	10	1.08766	0.53	54.40	119.4	0.000001	0.000091
PLANT B	25.41	REB 2	2	ACETONE	140000	0.04104	280.00	2.053	58	0.048253	0.099070
PLANT B	25.41	REB 2	2	TETRACHLOROETHENE	10	0.65670	0.32	32.85	165	0.000001	0.000039
PLANT B	25.41	REB 2	2	ETHYLBENZENE	41	0.27529	0.55	13.77	99	0.000008	0.000114
PLANT B	25.41	REB 2	2	METHYL ETHYL KETONE	1300	0.00789	0.50	0.394	72.1	0.000360	0.000142
PLANT B	25.41	REB 2	2	TRICHLOROETHANE 1,1,1	1100	0.00392	0.21	0.195	133	0.000165	0.000032
PLANT B	25.41	REB 2	2	TOLUENE	820	0.04505	1.80	2.253	92.1	0.000177	0.000401
PLANT B	25.41	REB 2	2	XYLENES	110	0.41044	2.20	20.53	106	0.000020	0.000425
PLANT B	25.41	REB 2	2	WATER	85.62%	601.86	25.11	0.030	18	0.950867	0.028627
PLANT B	25.41	REB 2	2	TOTAL ORGANICS	143821						
PLANT B	25.42	REB 3	2	ISOPROPANOL	110	0.00000		0	60	0.000033	0
PLANT B	25.42	REB 3	2	CHLOROFORM	10	2.46262	1.20	136.4	119.4	0.000001	0.000206
PLANT B	25.42	REB 3	2	ACETONE	4100	0.03554	7.10	1.968	58	0.001276	0.002512
PLANT B	25.42	REB 3	2	TETRACHLOROETHENE	10	0.80035	0.39	44.33	165	0.000001	0.000048
PLANT B	25.42	REB 3	2	ETHYLBENZENE	10	0.41044	0.20	22.73	99	0.000001	0.000041
PLANT B	25.42	REB 3	2	METHYL ETHYL KETONE	14	0.00000		0	72.1	0.000003	0
PLANT B	25.42	REB 3	2	TRICHLOROETHANE 1,1,1	32	0.31424	0.49	17.40	133	0.000004	0.000075
PLANT B	25.42	REB 3	2	TOLUENE	28	0.00000		0	92.1	0.000005	0
PLANT B	25.42	REB 3	2	XYLENES	10	0.75931	0.37	42.05	106	0.000001	0.000071
PLANT B	25.42	REB 3	2	WATER	99.57%	517.54	25.11	0.028	18	0.998671	0.028627
PLANT B	25.42	REB 3	2	TOTAL ORGANICS	4324						
PLANT B	25.43	REB 4	2	ISOPROPANOL	13	0.00000		0	60	0.000003	0
PLANT B	25.43	REB 4	2	CHLOROFORM	10	1.37496	0.67	76.34	119.4	0.000001	0.000115
PLANT B	25.43	REB 4	2	ACETONE	690	0.06246	2.10	3.468	58	0.000214	0.000743
PLANT B	25.43	REB 4	2	TRICHLOROETHANE 1,1,1	10	0.45148	0.22	25.06	133	0.000001	0.000033
PLANT B	25.43	REB 4	2	XYLENES	10	0.22574	0.11	12.53	106	0.000001	0.000021
PLANT B	25.43	REB 4	2	WATER	99.93%	515.68	25.11	0.028	18	0.999777	0.028627
PLANT B	25.43	REB 4	2	TOTAL ORGANICS	733						
PLANT B	25.44	DISTIL.	2	DICHLOROETHENE	10	1.08766	0.53	21.72	97	0.000005	0.000112
PLANT B	25.44	DISTIL.	2	DIMETHYL OXIRANE 2,2	10	0.57461	0.28	11.47	85	0.000005	0.000067
PLANT B	25.44	DISTIL.	2	ACETONE	840000	0.01099	450.00	0.219	58	0.725049	0.159221
PLANT B	25.44	DISTIL.	2	CHLOROFORM	10	2.46262	1.20	49.19	119.4	0.000004	0.000206
PLANT B	25.44	DISTIL.	2	BROMODICHLOROMETNANE	22000	0.00038	0.41	0.007	164	0.006715	0.000051
PLANT B	25.44	DISTIL.	2	METHYL ETHYL KETONE	10	0.43096	0.21	9.608	72.1	0.000006	0.000059
PLANT B	25.44	DISTIL.	2	TRICHLOROETHANE 1,1,1	11000	0.00095	0.51	0.019	133	0.004140	0.000078
PLANT B	25.44	DISTIL.	2	TRICHLOROETHENE	8000	0.00059	0.23	0.011	153.8	0.002604	0.000030
PLANT B	25.44	DISTIL.	2	TOLUENE	31000	0.00008	0.12	0.001	92.1	0.016850	0.000026
PLANT B	25.44	DISTIL.	2	DICHLOROPROPANE 1,2	10	0.20522	0.10	4.099	106	0.000004	0.000019

(CONTINUED)

TABLE A-1. (CONTINUED)

PLANT	SAMPLE NUMBER	LOC.	BATCH OR PROCESS	COMPONENT	LIQUID CONC. (mg/L)	H CONST. A/M*M3 *E-3	VAPOR CONC. (mg/L)	K (Y/X)	MOLECULAR WEIGHT	X	Y
PLANT B	25.44	DISTIL.	2	WATER	8.80%	5859.05	25.11	0.117	18	0.244612	0.028627
PLANT B	25.44	DISTIL.	2	TOTAL ORGANICS	912050						
PLANT C	ER1	FEED	TFE	ACETONE	743000	0.01044	378.00	0.135	58	0.986933	0.133745
PLANT C	ER1	FEED	TFE	FREON TF	1000	0.04104	2.00	0.532	186.3	0.000413	0.000220
PLANT C	ER1	FEED	TFE	TRICHLOROETHANE	15000	0.02449	17.90	0.317	133	0.008688	0.002761
PLANT C	ER1	FEED	TFE	TRICHLOROETHYLENE	2000	0.00103	0.10	0.013	131	0.001176	0.000015
PLANT C	ER1	FEED	TFE	TOLUENE	5000	0.00123	0.30	0.015	92.1	0.004182	0.000066
PLANT C	ER1	FEED	TFE	ETHYL BENZENE	0		0.10		106	0	0.000019
PLANT C	ER1	FEED	TFE	XYLENES	59000	0.00073	2.10	0.009	106	0.042881	0.000406
PLANT C	ER1	FEED	TFE	TETRACHLOROETHYLENE	6000	0.00821	2.40	0.106	165.8	0.002788	0.000297
PLANT C	ER1	FEED	TFE	TOTAL ORGANICS	831000						
PLANT C	ER2	DISTIL.	TFE	ACETONE	822000	0.00956	383.00	0.137	58	0.984451	0.135514
PLANT C	ER2	DISTIL.	TFE	FREON TF	1000	0.04104	2.00	0.590	186.3	0.000372	0.000220
PLANT C	ER2	DISTIL.	TFE	TRICHLOROETHANE	22000	0.01782	19.10	0.256	133	0.011490	0.002947
PLANT C	ER2	DISTIL.	TFE	TRICHLOROETHYLENE	3000	0.00068	0.10	0.009	131	0.001590	0.000015
PLANT C	ER2	DISTIL.	TFE	TOLUENE	9000	0.00046	0.20	0.006	92.1	0.006787	0.000044
PLANT C	ER2	DISTIL.	TFE	ETHYL BENZENE	3000	0.00068	0.10	0.009	106	0.001965	0.000019
PLANT C	ER2	DISTIL.	TFE	XYLENES	20000	0.00021	0.20	0.002	106	0.013106	0.000038
PLANT C	ER2	DISTIL.	TFE	TETRACHLOROETHYLENE	5000	0.00657	1.60	0.094	165.8	0.002094	0.000198
PLANT C	ER2	DISTIL.	TFE	TOTAL ORGANICS	885000						
PLANT C	ER3	FINAL	TFE	ACETONE	606000	0.01043	308.00	0.110	58	0.987248	0.108977
PLANT C	ER3	FINAL	TFE	FREON TF	1000	0.03078	1.50	0.325	186.3	0.000507	0.000165
PLANT C	ER3	FINAL	TFE	TRICHLOROETHANE	9000	0.02098	9.20	0.222	133	0.006394	0.001419
PLANT C	ER3	FINAL	TFE	TRICHLOROETHYLENE	1000	0.00205	0.10	0.021	131	0.000721	0.000015
PLANT C	ER3	FINAL	TFE	TOLUENE	3000	0.00274	0.40	0.028	92.1	0.003077	0.000089
PLANT C	ER3	FINAL	TFE	ETHYL BENZENE	1000	0.00205	0.10	0.021	106	0.000891	0.000019
PLANT C	ER3	FINAL	TFE	XYLENES	136000	0.00075	5.00	0.007	106	0.121231	0.000968
PLANT C	ER3	FINAL	TFE	TETRACHLOROETHYLENE	9000	0.00935	4.10	0.098	165.8	0.005129	0.000507
PLANT C	ER3	FINAL	TFE	TOTAL ORGANICS	766000						
PLANT A	10	PRODUCT	TFE	CHLOROFORM	0		0.14		119.3	0	0.000024
PLANT A	10	PRODUCT	TFE	METHYLENE CHLORID	9000	0.00221	0.97	0.011	85	0.020879	0.000234
PLANT A	10	PRODUCT	TFE	TOLUENE	16000	0.00005	0.04	0.000	92.1	0.034256	0.000008
PLANT A	10	PRODUCT	TFE	TRICHLOROETHANE	0		0.14		133	0	0.000021
PLANT A	10	PRODUCT	TFE	FREON TF	18000	0.00171	1.50	0.008	186.3	0.019052	0.000165
PLANT A	10	PRODUCT	TFE	HIGH BOILERS	939000	0.00000	0.00	0	200	0.925811	0
PLANT A	10	PRODUCT	TFE	TOTAL ORGANICS	982000						
PLANT A	11	FEED	TFE	CHLOROFORM	15000	0.00698	5.10	0.036	119.3	0.023836	0.000877
PLANT A	11	FEED	TFE	METHYLENE CHLORID	20000	0.00174	1.70	0.009	85	0.044607	0.000410
PLANT A	11	FEED	TFE	TOLUENE	13000	0.00002	0.01	0.000	92.1	0.026759	0.000002
PLANT A	11	FEED	TFE	TRICHLOROETHANE	7000	0.00032	0.11	0.001	133	0.009977	0.000016
PLANT A	11	FEED	TFE	FREON TF	0		0.06		186.3	0	0.000006
PLANT A	11	FEED	TFE	HIGH BOILERS	944000	0.00000	0.00	0	200	0.894818	0
PLANT A	11	FEED	TFE	TOTAL ORGANICS	999000						

(CONTINUED)

TABLE A-1. (CONTINUED)

PLANT	SAMPLE NUMBER	LOC.	BATCH OR PROCESS	COMPONENT	LIQUID CONC. (mg/L)	H CONST. A/M*M3 *E-3	VAPOR CONC. (mg/L)	K (Y/X)	MOLECULAR WEIGHT	X	Y
PLANT A	12	BOTTOMS	TFE	CHLOROFORM	0		0.01		119.3		0.000001
PLANT A	12	BOTTOMS	TFE	METHYLENE CHLORID	0		0.03		85		0.000007
PLANT A	12	BOTTOMS	TFE	TOLUENE	0		0.03		92.1		0.000006
PLANT A	12	BOTTOMS	TFE	TRICHLOROETHANE	0		0.01		133		0.000001
PLANT A	12	BOTTOMS	TFE	FREON TF	0		0.24		186.3		0.000026
PLANT A	12	BOTTOMS	TFE	TOTAL ORGANICS	0						
PLANT B	21	FEED #2	TFE	ISOPROPANOL	382000	0.00004	0.75	0.000	60	0.522794	0.000256
PLANT B	21	FEED #2	TFE	FREON TF	6000	0.12997	38.00	1.582	186.3	0.002644	0.004185
PLANT B	21	FEED #2	TFE	TOLUENE	4000	0.00298	0.58	0.036	92.1	0.003566	0.000129
PLANT B	21	FEED #2	TFE	ETHYL BENZENE	116000	0.00097	5.50	0.011	106	0.089860	0.001064
PLANT B	21	FEED #2	TFE	XYLENES	492000	0.00092	22.00	0.011	106	0.381134	0.004259
PLANT B	21	FEED #2	TFE	TOTAL ORGANICS	1000000						
PLANT B	22	FEED #1	TFE	ISOPROPANOL	429000	0.00003	0.69	0.000	60	0.571914	0.000236
PLANT B	22	FEED #1	TFE	FREON TF	5000	0.11903	29.00	1.488	186.3	0.002146	0.003194
PLANT B	22	FEED #1	TFE	TOLUENE	3000	0.00328	0.48	0.041	92.1	0.002605	0.000106
PLANT B	22	FEED #1	TFE	ETHYL BENZENE	104000	0.00114	5.80	0.014	106	0.078478	0.001122
PLANT B	22	FEED #1	TFE	XYLENES	457000	0.00103	23.00	0.012	106	0.344854	0.004452
PLANT B	22	FEED #1	TFE	TOTAL ORGANICS	998000						
PLANT B	25	PROD. #1	TFE	ISOPROPANOL	538000	0.00004	1.10	0.000	60	0.687223	0.000376
PLANT B	25	PROD. #1	TFE	FREON TF	7000	0.18176	62.00	2.371	186.3	0.002879	0.006829
PLANT B	25	PROD. #1	TFE	TOLUENE	4000	0.00482	0.94	0.062	92.1	0.003328	0.000209
PLANT B	25	PROD. #1	TFE	ETHYL BENZENE	84000	0.00129	5.30	0.016	106	0.060735	0.001026
PLANT B	25	PROD. #1	TFE	XYLENES	340000	0.00115	19.00	0.014	106	0.245832	0.003678
PLANT B	25	PROD. #1	TFE	TOTAL ORGANICS	973000						
PLANT B	26	PROD. #2	TFE	ISOPROPANOL	603000	0.00004	1.10	0.000	60	0.751631	0.000376
PLANT B	26	PROD. #2	TFE	FREON TF	6000	0.17444	51.00	2.332	186.3	0.002408	0.005617
PLANT B	26	PROD. #2	TFE	TOLUENE	4000	0.00364	0.71	0.048	92.1	0.003248	0.000158
PLANT B	26	PROD. #2	TFE	ETHYL BENZENE	70000	0.00141	4.80	0.018	106	0.049389	0.000929
PLANT B	26	PROD. #2	TFE	XYLENES	274000	0.00127	17.00	0.017	106	0.193322	0.003291
PLANT B	26	PROD. #2	TFE	TOTAL ORGANICS	957000						
PLANT D	45.03	A WASTE	1	METHYLENE CHLORIDE	0		0.17		85	0	0.000041
PLANT D	45.03	A WASTE	1	ACETONE	39	0.05788	0.11	3.203	58	0.000012	0.000038
PLANT D	45.03	A WASTE	1	ISOPROPANOL	960	0.01133	0.53	0.626	60	0.000289	0.000181
PLANT D	45.03	A WASTE	1	METHYL ETHYL KETONE	1040	0.08288	4.20	4.586	72.1	0.000260	0.001195
PLANT D	45.03	A WASTE	1	TRICHLOROETHANE	170	0.47079	3.90	26.05	133	0.000023	0.000601
PLANT D	45.03	A WASTE	1	TRICHLOROETHYLENE	0		0.61		131	0	0.000095
PLANT D	45.03	A WASTE	1	TETRACHLOROETHYLENE	290	0.09199	1.30	5.090	165.8	0.000031	0.000160
PLANT D	45.03	A WASTE	1	ETHYL BENZENE	360	0.26222	4.60	14.51	106	0.000061	0.000890
PLANT D	45.03	A WASTE	1	TOLUENE	86	1.93287	8.10	106.9	92.1	0.000016	0.001804
PLANT D	45.03	A WASTE	1	XYLENES	2000	0.16417	16.00	9.085	106	0.000340	0.003097
PLANT D	45.03	A WASTE	1	WATER	99.51%	517.86	25.11	0.028	18	0.998964	0.028627
PLANT D	45.03	A WASTE	1	TOTAL ORGANICS	4945						
PLANT D	45.05	MST	1	ACETONE	12	0.17102	0.10	9.482	58	0.000003	0.000035

(CONTINUED)

TABLE A-1. (CONTINUED)

PLANT	SAMPLE NUMBER	LOC.	BATCH OR PROCESS	COMPONENT	LIQUID CONC. (mg/L)	H CONST. A/M*M3 *E-3	VAPOR CONC. (mg/L)	K (Y/X)	MOLECULAR WEIGHT	X	Y
PLANT D	45.05	MST	1	ISOPROPANOL	640	0.00513	0.16	0.284	60	0.000192	0.000054
PLANT D	45.05	MST	1	METHYL ETHYL KETONE	460	0.03301	0.74	1.830	72.1	0.000115	0.000210
PLANT D	45.05	MST	1	TRICHLOROETHANE	99	0.04975	0.24	2.758	133	0.000013	0.000037
PLANT D	45.05	MST	1	TRICHLOROETHYLENE	0		0.34		131	0	0.000053
PLANT D	45.05	MST	1	TETRACHLOROETHYLENE	230	0.05889	0.66	3.265	165.8	0.000025	0.000081
PLANT D	45.05	MST	1	ETHYL BENZENE	560	0.16857	4.60	9.346	106	0.000095	0.000890
PLANT D	45.05	MST	1	TOLUENE	32	3.59132	5.60	199.1	92.1	0.000006	0.001247
PLANT D	45.05	MST	1	XYLENES	480	0.72681	17.00	40.29	106	0.000081	0.003291
PLANT D	45.05	MST	1	WATER	99.75%	516.60	25.11	0.028	18	0.999467	0.028627
PLANT D	45.05	MST	1	TOTAL ORGANICS	2513						
PLANT D	45.06	STRIP. 3	1	ISOPROPANOL	47	0.04366	0.10	2.424	60	0.000014	0.000034
PLANT D	45.06	STRIP. 3	1	METHYL ETHYL KETONE	70	0.03694	0.13	2.050	72.1	0.000017	0.000035
PLANT D	45.06	STRIP. 3	1	TRICHLOROETHANE	33	0.06219	0.10	3.452	133	0.000004	0.000015
PLANT D	45.06	STRIP. 3	1	TETRACHLOROETHYLENE	72	0.02850	0.10	1.582	165.8	0.000007	0.000012
PLANT D	45.06	STRIP. 3	1	ETHYL BENZENE	56	0.19422	0.53	10.78	106	0.000009	0.000102
PLANT D	45.06	STRIP. 3	1	TOLUENE	17	0.14486	0.12	8.043	92.1	0.000003	0.000026
PLANT D	45.06	STRIP. 3	1	XYLENES	410	0.12013	2.40	6.669	106	0.000069	0.000464
PLANT D	45.06	STRIP. 3	1	WATER	99.93%	515.67	25.11	0.028	18	0.999873	0.028627
PLANT D	45.06	STRIP. 3	1	TOTAL ORGANICS	705						
PLANT D	45.07	STRIP. 4	1	METHYL ETHYL KETONE	34	0.03984	0.07	2.212	72.1	0.000008	0.000018
PLANT D	45.07	STRIP. 4	1	ETHYL BENZENE	100	0.12108	0.59	6.724	106	0.000016	0.000114
PLANT D	45.07	STRIP. 4	1	TOLUENE	42	0.20522	0.42	11.39	92.1	0.000008	0.000093
PLANT D	45.07	STRIP. 4	1	XYLENES	270	0.13681	1.80	7.597	106	0.000045	0.000348
PLANT D	45.07	STRIP. 4	1	WATER	99.96%	515.53	25.11	0.028	18	0.999920	0.028627
PLANT D	45.07	STRIP. 4	1	TOTAL ORGANICS	446						
PLANT D	45.08	MST	1	METHYLENE CHLORIDE	0		0.20		85	0	0.000048
PLANT D	45.08	MST	1	ACETONE	350	0.02404	0.41	1.316	58	0.000110	0.000145
PLANT D	45.08	MST	1	ISOPROPANOL	11000	0.04664	25.00	2.554	60	0.003346	0.008550
PLANT D	45.08	MST	1	METHYL ETHYL KETONE	6600	0.03482	11.20	1.907	72.1	0.001671	0.003187
PLANT D	45.08	MST	1	TRICHLOROETHANE	1100	0.00802	0.43	0.439	133	0.000150	0.000066
PLANT D	45.08	MST	1	TETRACHLOROETHYLENE	160	0.26935	2.10	14.75	165.8	0.000017	0.000259
PLANT D	45.08	MST	1	ETHYL BENZENE	0		0.65		106	0	0.000125
PLANT D	45.08	MST	1	XYLENES	25	0.29551	0.36	16.18	106	0.000004	0.000069
PLANT D	45.08	MST	1	WATER	98.08%	525.41	25.11	0.028	18	0.994698	0.028627
PLANT D	45.08	MST	1	TOTAL ORGANICS	19235						
PLANT D	45.09	PRODUCT	1	METHYLENE CHLORIDE			0.77		85	0	0.000185
PLANT D	45.09	PRODUCT	1	ACETONE	0		0.45		58	0	0.000159
PLANT D	45.09	PRODUCT	1	ISOPROPANOL			1.80		60	0	0.000615
PLANT D	45.09	PRODUCT	1	METHYL ETHYL KETONE			55.00		72.1	0	0.015654
PLANT D	45.09	PRODUCT	1	TRICHLOROETHANE		0	2.50		133	0	0.000385
PLANT D	45.09	PRODUCT	1	TRICHLOROETHYLENE		0	2.00		131	0	0.000313
PLANT D	45.09	PRODUCT	1	TETRACHLOROETHYLENE			3.30		165.8	0	0.000408
PLANT D	45.09	PRODUCT	1	ETHYL BENZENE			5.10		106	0	0.000987

(CONTINUED)

TABLE A-1. (CONTINUED)

PLANT	SAMPLE NUMBER	LOC.	BATCH OR PROCESS	COMPONENT	LIQUID CONC. (mg/L)	H CONST. A/M*M3 *E-3	VAPOR CONC. (mg/L)	K (Y/X)	MOLECULAR WEIGHT	X	Y
PLANT D	45.09	PRODUCT	1	TOLUENE			13.00		92.1	0	0.002896
PLANT D	45.09	PRODUCT	1	XYLENES		300000	16.00		106	0	0.003097
PLANT D	45.09	PRODUCT	1	WATER	100.00%	515.30	25.11	0.028	18	1	0.028627
PLANT D	45.09	PRODUCT	1	TOTAL ORGANICS	0						
PLANT D	45.10	MST	1	METHYLENE CHLORIDE	0		1.80		85	0	0.000434
PLANT D	45.10	MST	1	ACETONE	1000	0.02463	1.20	1.321	58	0.000321	0.000424
PLANT D	45.10	MST	1	ISOPROPANOL	27000	0.00418	5.50	0.224	60	0.008386	0.001881
PLANT D	45.10	MST	1	METHYL ETHYL KETONE	16600	0.03214	26.00	1.724	72.1	0.004290	0.007400
PLANT D	45.10	MST	1	TRICHLOROETHANE	2100	0.02150	2.20	1.153	133	0.000294	0.000339
PLANT D	45.10	MST	1	TRICHLOROETHYLENE	0		1.30		131	0	0.000203
PLANT D	45.10	MST	1	TETRACHLOROETHYLENE	260	0.00789	0.10	0.423	165.8	0.000029	0.000012
PLANT D	45.10	MST	1	ETHYL BENZENE	0		5.20		106	0	0.001006
PLANT D	45.10	MST	1	TOLUENE	3	75.24671	11.00	4037.	92.1	0.000000	0.002451
PLANT D	45.10	MST	1	XYLENES	11	31.71555	17.00	1701.	106	0.000001	0.003291
PLANT D	45.10	MST	1	WATER	95.30%	540.70	25.11	0.029	18	0.986676	0.028627
PLANT D	45.10	MST	1	TOTAL ORGANICS	46974						
PLANT D	45.11	A WASTE	4	METHYLENE CHLORIDE	0		0.63		85	0	0.000152
PLANT D	45.11	A WASTE	4	ACETONE	6500	0.02684	8.50	1.480	58	0.002030	0.003007
PLANT D	45.11	A WASTE	4	ISOPROPANOL	95	0.02160	0.10	1.192	60	0.000028	0.000034
PLANT D	45.11	A WASTE	4	METHYL ETHYL KETONE	112	0.05863	0.32	3.235	72.1	0.000028	0.000091
PLANT D	45.11	A WASTE	4	TRICHLOROETHANE	2200	0.17723	19.00	9.780	133	0.000299	0.002931
PLANT D	45.11	A WASTE	4	TRICHLOROETHYLENE	0		1.90		131	0	0.000297
PLANT D	45.11	A WASTE	4	TETRACHLOROETHYLENE	55	0.63431	1.70	35.00	165.8	0.000006	0.000210
PLANT D	45.11	A WASTE	4	ETHYL BENZENE	86	1.02609	4.30	56.62	106	0.000014	0.000832
PLANT D	45.11	A WASTE	4	TOLUENE	86	1.81356	7.60	100.0	92.1	0.000016	0.001693
PLANT D	45.11	A WASTE	4	XYLENES	0		15.00		106	0	0.002904
PLANT D	45.11	A WASTE	4	WATER	99.09%	520.05	25.11	0.028	18	0.997574	0.028627
PLANT D	45.11	A WASTE	4	TOTAL ORGANICS	9134						
PLANT D	45.13	CONDEN.	4	METHYLENE CHLORIDE	0		0.83		85	0	0.000200
PLANT D	45.13	CONDEN.	4	ACETONE	32000	0.01924	30.00	1.008	58	0.010523	0.010614
PLANT D	45.13	CONDEN.	4	ISOPROPANOL	380	0.00540	0.10	0.283	60	0.000120	0.000034
PLANT D	45.13	CONDEN.	4	METHYL ETHYL KETONE	420	0.05961	1.22	3.125	72.1	0.000111	0.000347
PLANT D	45.13	CONDEN.	4	TRICHLOROETHANE	16000	0.03976	31.00	2.084	133	0.002294	0.004783
PLANT D	45.13	CONDEN.	4	TRICHLOROETHYLENE	120	0.23942	1.40	12.55	131	0.000017	0.000219
PLANT D	45.13	CONDEN.	4	TETRACHLOROETHYLENE	1100	0.02425	1.30	1.271	165.8	0.000126	0.000160
PLANT D	45.13	CONDEN.	4	ETHYL BENZENE	3400	0.02113	3.50	1.107	106	0.000611	0.000677
PLANT D	45.13	CONDEN.	4	TOLUENE	2200	0.05504	5.90	2.885	92.1	0.000455	0.001314
PLANT D	45.13	CONDEN.	4	XYLENES	17000	0.01449	12.00	0.759	106	0.003058	0.002323
PLANT D	45.13	CONDEN.	4	WATER	92.74%	555.65	25.11	0.029	18	0.982679	0.028627
PLANT D	45.13	CONDEN.	4	TOTAL ORGANICS	72620						
PLANT D	45.14	CONDEN.	4	METHYLENE CHLORIDE	0		0.25		85	0	0.000060
PLANT D	45.14	CONDEN.	4	ACETONE	130	0.02526	0.16	1.366	58	0.000041	0.000056
PLANT D	45.14	CONDEN.	4	METHYL ETHYL KETONE	11	0.61953	0.32	33.51	72.1	0.000002	0.000091

(CONTINUED)

TABLE A-1. (CONTINUED)

PLANT	SAMPLE NUMBER	LOC.	BATCH OR PROCESS	COMPONENT	LIQUID CONC. (mg/L)	H CONST. A/M*M3 *E-3	VAPOR CONC. (mg/L)	K (Y/X)	MOLECULAR WEIGHT	X	Y
PLANT D	45.14	CONDEN.	4	TRICHLOROETHANE	2900	0.21229	30.00	11.48	133	0.000403	0.004628
PLANT D	45.14	CONDEN.	4	TRICHLOROETHYLENE	0		1.10		131	0	0.000172
PLANT D	45.14	CONDEN.	4	TETRACHLOROETHYLENE	420	0.04886	1.00	2.643	165.8	0.000046	0.000123
PLANT D	45.14	CONDEN.	4	ETHYL BENZENE	26000	0.00245	3.10	0.132	106	0.004534	0.000600
PLANT D	45.14	CONDEN.	4	TOLUENE	530	0.17037	4.40	9.215	92.1	0.000106	0.000980
PLANT D	45.14	CONDEN.	4	XYLENES	1600	0.14109	11.00	7.631	106	0.000279	0.002129
PLANT D	45.14	CONDEN.	4	WATER	96.84%	532.11	25.11	0.028	18	0.994586	0.028627
PLANT D	45.14	CONDEN.	4	TOTAL ORGANICS	31591						
PLANT D	45.15	STRIP. 2	4	ACETONE	270	0.02508	0.33	1.390	58	0.000083	0.000116
PLANT D	45.15	STRIP. 2	4	METHYL ETHYL KETONE	7	0.54322	0.18	30.11	72.1	0.000001	0.000051
PLANT D	45.15	STRIP. 2	4	TRICHLOROETHANE	930	0.00221	0.10	0.122	133	0.000126	0.000015
PLANT D	45.15	STRIP. 2	4	TRICHLOROETHYLENE	0		0.26		131	0	0.000040
PLANT D	45.15	STRIP. 2	4	ETHYL BENZENE	300	0.04652	0.68	2.578	106	0.000051	0.000131
PLANT D	45.15	STRIP. 2	4	TOLUENE	170	0.05674	0.47	3.145	92.1	0.000033	0.000104
PLANT D	45.15	STRIP. 2	4	XYLENES	900	0.06385	2.80	3.539	106	0.000153	0.000542
PLANT D	45.15	STRIP. 2	4	WATER	99.74%	516.63	25.11	0.028	18	0.999550	0.028627
PLANT D	45.15	STRIP. 2	4	TOTAL ORGANICS	2577						
PLANT D	45.16	STRIP. 3	4	ACETONE	32	0.10902	0.17	6.051	58	0.000009	0.000060
PLANT D	45.16	STRIP. 3	4	METHYL ETHYL KETONE	7	0.72430	0.24	40.20	72.1	0.000001	0.000068
PLANT D	45.16	STRIP. 3	4	TRICHLOROETHANE	460	0.04015	0.90	2.228	133	0.000062	0.000138
PLANT D	45.16	STRIP. 3	4	TRICHLOROETHYLENE	0		0.57		131	0	0.000089
PLANT D	45.16	STRIP. 3	4	ETHYL BENZENE	190	0.03240	0.30	1.798	106	0.000032	0.000058
PLANT D	45.16	STRIP. 3	4	TOLUENE	56	0.05130	0.14	2.847	92.1	0.000010	0.000031
PLANT D	45.16	STRIP. 3	4	XYLENES	310	0.06620	1.00	3.674	106	0.000052	0.000193
PLANT D	45.16	STRIP. 3	4	WATER	99.89%	515.85	25.11	0.028	18	0.999830	0.028627
PLANT D	45.16	STRIP. 3	4	TOTAL ORGANICS	1055						
PLANT D	45.17	STRIP. 4	4	TRICHLOROETHANE	230	0.15168	1.70	8.423	133	0.000031	0.000262
PLANT D	45.17	STRIP. 4	4	TRICHLOROETHYLENE	0		0.28		131	0	0.000043
PLANT D	45.17	STRIP. 4	4	ETHYL BENZENE	35	0.19349	0.33	10.74	106	0.000005	0.000063
PLANT D	45.17	STRIP. 4	4	TOLUENE	35	0.05863	0.10	3.256	92.1	0.000006	0.000022
PLANT D	45.17	STRIP. 4	4	XYLENES	120	0.09919	0.58	5.508	106	0.000020	0.000112
PLANT D	45.17	STRIP. 4	4	WATER	99.96%	515.52	25.11	0.028	18	0.999935	0.028627
PLANT D	45.17	STRIP. 4	4	TOTAL ORGANICS	420						
PLANT D	45.20	MST	4	METHYLENE CHLORIDE	0		1.00		85	0	0.000241
PLANT D	45.20	MST	4	ACETONE	23000	0.02409	27.00	1.304	58	0.007324	0.009553
PLANT D	45.20	MST	4	ISOPROPANOL	250	0.07388	0.90	3.999	60	0.000076	0.000307
PLANT D	45.20	MST	4	METHYL ETHYL KETONE	400	0.05336	1.04	2.888	72.1	0.000102	0.000296
PLANT D	45.20	MST	4	TRICHLOROETHANE	10000	0.07798	38.00	4.221	133	0.001388	0.005863
PLANT D	45.20	MST	4	TRICHLOROETHYLENE	0		2.00		131	0	0.000313
PLANT D	45.20	MST	4	TETRACHLOROETHYLENE	210	0.22476	2.30	12.16	165.8	0.000023	0.000284
PLANT D	45.20	MST	4	ETHYL BENZENE	69	1.30864	4.40	70.84	106	0.000012	0.000851
PLANT D	45.20	MST	4	TOLUENE	23	7.76260	8.70	420.2	92.1	0.000004	0.001938
PLANT D	45.20	MST	4	XYLENES	320	0.96196	15.00	52.07	106	0.000055	0.002904

(CONTINUED)

TABLE A-1. (CONTINUED)

PLANT	SAMPLE NUMBER	LOC.	BATCH OR PROCESS	COMPONENT	LIQUID CONC. (mg/L)	H CONST. A/M*M3 *E-3	VAPOR CONC. (mg/L)	K (Y/X)	MOLECULAR WEIGHT	X	Y
PLANT D	45.20	MST	4	WATER	96.57%	533.59	25.11	0.028	18	0.991011	0.028627
PLANT D	45.20	MST	4	TOTAL ORGANICS	34272						
PLANT D	45.21	PRODUCT	4	METHYLENE CHLORIDE	0		1.40		85	0	0.000338
PLANT D	45.21	PRODUCT	4	ACETONE	0		20.00		58	0	0.007076
PLANT D	45.21	PRODUCT	4	METHYL ETHYL KETONE	0		10.00		72.1	0	0.002846
PLANT D	45.21	PRODUCT	4	TRICHLOROETHANE	40000	0.02822	55.00	1.070	133	0.007930	0.008486
PLANT D	45.21	PRODUCT	4	TRICHLOROETHYLENE	4000	0.01539	3.00	0.583	131	0.000805	0.000469
PLANT D	45.21	PRODUCT	4	TETRACHLOROETHYLENE	6000	0.01026	3.00	0.389	165.8	0.000954	0.000371
PLANT D	45.21	PRODUCT	4	ETHYL BENZENE	60000	0.00239	7.00	0.090	106	0.014925	0.001355
PLANT D	45.21	PRODUCT	4	TOLUENE	0		13.00		92.1	0	0.002896
PLANT D	45.21	PRODUCT	4	XYLENES	270000	0.00198	26.00	0.074	106	0.067163	0.005033
PLANT D	45.21	PRODUCT	4	WATER	62.00%	831.13	25.11	0.031	18	0.908222	0.028627
PLANT D	45.21	PRODUCT	4	TOTAL ORGANICS	380000						
PLANT D	45.22	A WASTE	2	METHYLENE CHLORIDE	0		0.41		85	0	0.000098
PLANT D	45.22	A WASTE	2	ACETONE	0		0.28		58	0	0.000099
PLANT D	45.22	A WASTE	2	METHYL ETHYL KETONE	75000	0.14228	520.00	2.948	72.1	0.050192	0.148007
PLANT D	45.22	A WASTE	2	TRICHLOROETHANE	660000	0.01368	440.00	0.283	133	0.239442	0.067891
PLANT D	45.22	A WASTE	2	TETRACHLOROETHYLENE	0		0.10		165.8	0	0.000012
PLANT D	45.22	A WASTE	2	TOLUENE	0		0.10		92.1	0	0.000022
PLANT D	45.22	A WASTE	2	WATER	26.50%	1944.54	25.11	0.040	18	0.710365	0.028627
PLANT D	45.22	A WASTE	2	TOTAL ORGANICS	735000						
PLANT D	45.24	A WASTE	2	ACETONE	0		0.18		58	0	0.000063
PLANT D	45.24	A WASTE	2	METHYL ETHYL KETONE	0		4.10		72.1	0	0.001166
PLANT D	45.24	A WASTE	2	TRICHLOROETHANE	0		460.00		133	0	0.070977
PLANT D	45.24	A WASTE	2	WATER	100.00%	515.30	25.11	0.028	18	1	0.028627
PLANT D	45.24	A WASTE	2	TOTAL ORGANICS	0						
PLANT D	45.25	STRIP. 3	2	METHYL ETHYL KETONE	7	0.09657	0.03	5.262	72.1	0.000001	0.000009
PLANT D	45.25	STRIP. 3	2	TRICHLOROETHANE	22000	0.00541	5.80	0.294	133	0.003035	0.000894
PLANT D	45.25	STRIP. 3	2	ETHYL BENZENE	130	0.01579	0.10	0.860	106	0.000022	0.000019
PLANT D	45.25	STRIP. 3	2	TOLUENE	44	0.04664	0.10	2.541	92.1	0.000008	0.000022
PLANT D	45.25	STRIP. 3	2	WATER	97.78%	526.99	25.11	0.028	18	0.996931	0.028627
PLANT D	45.25	STRIP. 3	2	TOTAL ORGANICS	22181						
PLANT D	45.26	STRIP. 4	2	TRICHLOROETHANE	4100	0.00455	0.91	0.252	133	0.000556	0.000140
PLANT D	45.26	STRIP. 4	2	ETHYL BENZENE	56	0.03665	0.10	2.028	106	0.000009	0.000019
PLANT D	45.26	STRIP. 4	2	TOLUENE	23	0.08923	0.10	4.939	92.1	0.000004	0.000022
PLANT D	45.26	STRIP. 4	2	WATER	99.58%	517.47	25.11	0.028	18	0.999429	0.028627
PLANT D	45.26	STRIP. 4	2	TOTAL ORGANICS	4179						
PLANT D	45.27	MST	2	METHYLENE CHLORIDE	0		0.28		85	0	0.000067
PLANT D	45.27	MST	2	METHYL ETHYL KETONE	4000	0.12826	25.00	3.595	72.1	0.001979	0.007115
PLANT D	45.27	MST	2	TRICHLOROETHANE	560000	0.01686	460.00	0.472	133	0.150208	0.070977
PLANT D	45.27	MST	2	TRICHLOROETHYLENE	0		0.31		131	0	0.000048
PLANT D	45.27	MST	2	TETRACHLOROETHYLENE	0		0.10		165.8	0	0.000012
PLANT D	45.27	MST	2	ETHYL BENZENE	7000	0.00053	0.18	0.014	106	0.002355	0.000034

(CONTINUED)

TABLE A-1. (CONTINUED)

PLANT	SAMPLE NUMBER	LOC.	BATCH OR PROCESS	COMPONENT	LIQUID CONC. (mg/L)	H CONST. A/M*M3 *E-3	VAPOR CONC. (mg/L)	K (Y/X)	MOLECULAR WEIGHT	X	Y
PLANT D	45.27	MST	2	TOLUENE	3000	0.00123	0.18	0.034	92.1	0.001162	0.000040
PLANT D	45.27	MST	2	XYLENES	0		0.74		106	0	0.000143
PLANT D	45.27	MST	2	WATER	42.60%	1209.63	25.11	0.033	18	0.844294	0.028627
PLANT D	45.27	MST	2	TOTAL ORGANICS	574000						
PLANT D	45.28	PRODUCT	2	METHYLENE CHLORIDE	0		0.88		85	0	0.000212
PLANT D	45.28	PRODUCT	2	ACETONE	0		0.45		58	0	0.000159
PLANT D	45.28	PRODUCT	2	METHYL ETHYL KETONE	37000	0.20522	370.00	3.481	72.1	0.030245	0.105313
PLANT D	45.28	PRODUCT	2	TRICHLOROETHANE	770000	0.01492	560.00	0.253	133	0.341224	0.086407
PLANT D	45.28	PRODUCT	2	TRICHLOROETHYLENE	0		0.15		131	0	0.000023
PLANT D	45.28	PRODUCT	2	TETRACHLOROETHYLENE	0		0.10		165.8	0	0.000012
PLANT D	45.28	PRODUCT	2	TOLUENE	1300	0.00158	0.10	0.026	92.1	0.000831	0.000022
PLANT D	45.28	PRODUCT	2	WATER	19.17%	2688.07	25.11	0.045	18	0.627697	0.028627
PLANT D	45.28	PRODUCT	2	TOTAL ORGANICS	808300						
PLANT D	45.29	O WASTE	3	METHYLENE CHLORIDE	0		0.23		85	0	0.000055
PLANT D	45.29	O WASTE	3	ACETONE	290	0.01557	0.22	0.729	58	0.000106	0.000077
PLANT D	45.29	O WASTE	3	ISOPROPANOL	37	0.05546	0.10	2.597	60	0.000013	0.000034
PLANT D	45.29	O WASTE	3	METHYL ETHYL KETONE	1600	0.70544	55.00	33.03	72.1	0.000473	0.015654
PLANT D	45.29	O WASTE	3	TRICHLOROETHANE	180000	0.05016	440.00	2.349	133	0.028902	0.067891
PLANT D	45.29	O WASTE	3	TRICHLOROETHYLENE	0		0.30		131	0	0.000046
PLANT D	45.29	O WASTE	3	ETHYL BENZENE	44	0.11194	0.24	5.241	106	0.000008	0.000046
PLANT D	45.29	O WASTE	3	TOLUENE	6	0.85508	0.25	40.03	92.1	0.000001	0.000055
PLANT D	45.29	O WASTE	3	XYLENES	27	0.62326	0.82	29.18	106	0.000005	0.000158
PLANT D	45.29	O WASTE	3	WATER	81.80%	629.96	25.11	0.029	18	0.970488	0.028627
PLANT D	45.29	O WASTE	3	TOTAL ORGANICS	182004						
PLANT D	45.31	STRIP. 2	3	ACETONE	71	0.02890	0.10	1.506	58	0.000023	0.000035
PLANT D	45.31	STRIP. 2	3	METHYL ETHYL KETONE	250	0.08209	1.00	4.279	72.1	0.000066	0.000284
PLANT D	45.31	STRIP. 2	3	TRICHLOROETHANE	71000	0.00694	24.00	0.361	133	0.010240	0.003703
PLANT D	45.31	STRIP. 2	3	TRICHLOROETHYLENE	0		0.13		131	0	0.000020
PLANT D	45.31	STRIP. 2	3	ETHYL BENZENE	30	0.23258	0.34	12.12	106	0.000005	0.000065
PLANT D	45.31	STRIP. 2	3	XYLENES	45	0.35571	0.78	18.54	106	0.000008	0.000151
PLANT D	45.31	STRIP. 2	3	WATER	92.86%	554.92	25.11	0.028	18	0.989655	0.028627
PLANT D	45.31	STRIP. 2	3	TOTAL ORGANICS	71396						
PLANT D	45.32	STRIP. 3	3	TRICHLOROETHANE	28000	0.00344	4.70	0.186	133	0.003883	0.000725
PLANT D	45.32	STRIP. 3	3	ETHYL BENZENE	24	0.24797	0.29	13.44	106	0.000004	0.000056
PLANT D	45.32	STRIP. 3	3	WATER	97.20%	530.16	25.11	0.028	18	0.996112	0.028627
PLANT D	45.32	STRIP. 3	3	TOTAL ORGANICS	28024						
PLANT D	45.33	STRIP. 4	3	TRICHLOROETHANE	12000	0.00359	2.10	0.197	133	0.001641	0.000324
PLANT D	45.33	STRIP. 4	3	ETHYL BENZENE	12	0.17102	0.10	9.402	106	0.000002	0.000019
PLANT D	45.33	STRIP. 4	3	XYLENES	0		0.14		106	0	0.000027
PLANT D	45.33	STRIP. 4	3	WATER	98.80%	521.57	25.11	0.028	18	0.998356	0.028627
PLANT D	45.33	STRIP. 4	3	TOTAL ORGANICS	12012						
PLANT D	45.34	MST	3	METHYLENE CHLORIDE	33	0.16791	0.27	4.756	85	0.000013	0.000065
PLANT D	45.34	MST	3	ACETONE	1100	0.01213	0.65	0.343	58	0.000669	0.000229

(CONTINUED)

TABLE A-1. (CONTINUED)

PLANT	SAMPLE NUMBER	LOC.	BATCH OR PROCESS	COMPONENT	LIQUID CONC. (mg/L)	H CONST. A/M*M3 *E-3	VAPOR CONC. (mg/L)	K (Y/X)	MOLECULAR WEIGHT	X	Y
PLANT D	45.34	MST	3	ISOPROPANOL	160	0.01283	0.10	0.363	60	0.000094	0.000034
PLANT D	45.34	MST	3	METHYL ETHYL KETONE	6000	0.11629	34.00	3.294	72.1	0.002937	0.009677
PLANT D	45.34	MST	3	TRICHLOROETHANE	560000	0.01246	340.00	0.352	133	0.148630	0.052461
PLANT D	45.34	MST	3	TRICHLOROETHYLENE	0		0.21		131	0	0.000032
PLANT D	45.34	MST	3	ETHYL BENZENE	35	0.11727	0.20	3.322	106	0.000011	0.000038
PLANT D	45.34	MST	3	TOLUENE	480	0.01026	0.24	0.290	92.1	0.000183	0.000053
PLANT D	45.34	MST	3	XYLENES	67	0.20216	0.66	5.726	106	0.000022	0.000127
PLANT D	45.34	MST	3	WATER	43.21%	1192.49	25.11	0.033	18	0.847437	0.028627
PLANT D	45.34	MST	3	TOTAL ORGANICS	567875						
PLANT D	45.35	PRODUCT	3	METHYLENE CHLORIDE	0		0.89		85	0	0.000214
PLANT D	45.35	PRODUCT	3	ACETONE	0		0.49		58	0	0.000173
PLANT D	45.35	PRODUCT	3	METHYL ETHYL KETONE	14000	0.17590	120.00	3.070	72.1	0.011125	0.034155
PLANT D	45.35	PRODUCT	3	TRICHLOROETHANE	730000	0.01771	630.00	0.309	133	0.314484	0.097208
PLANT D	45.35	PRODUCT	3	TRICHLOROETHYLENE	0		0.40		131	0	0.000062
PLANT D	45.35	PRODUCT	3	TETRACHLOROETHYLENE	6000	0.00034	[illegible]	0.005	165.8	0.002073	0.000012
PLANT D	45.35	PRODUCT	3	ETHYL BENZENE	38000	0.00010	0.19	0.001	106	0.020540	0.000036
PLANT D	45.35	PRODUCT	3	TOLUENE	9000	0.00064	0.28	0.011	92.1	0.005599	0.000062
PLANT D	45.35	PRODUCT	3	XYLENES	0		0.51		106	0	0.000098
PLANT D	45.35	PRODUCT	3	WATER	20.30%	2538.44	25.11	0.044	18	0.646177	0.028627
PLANT D	45.35	PRODUCT	3	TOTAL ORGANICS	797000						

APPENDIX B

SUMMARY OF PROCESS DATA

This section presents a series of tables listing process information obtained at Plants B and D during the field evaluation procedures. These tables provide supplemental information to the information provided in Sections 8 and 9.

TABLE B-1. PROCESS DATA AT PLANT B
Aqueous Methyl Ethyl Ketone Batch

Initial batch charge	30,000 L	8,000 gal.
Steam flow rate[1]	820-900 kg/hr	1,800-2,000 lb/hr
Process time		15 hr
Distillation time		12 hr

Time	Batch (reboiler) Temp. °C	Column head Temp. °C	Reflux GPM	
06:30 A	18	-	-	Started heatup.
08:30 A	80	65	-	Batch on total reflux.
08:45 A	84	75	-	Batch on total reflux.
09:00 A	87	73	-	Batch on total reflux.
09:30 A	90	72	-	Started distillation.
10:00 A	89	68	14.8	
10:30 A	90	70	14.8	
11:00 A	90	72	14.8	
11:30 A	91	73	11.7	
12:00 A	92	72	-	
12:30 P	95	74	-	
01:00 P	98	74	10.1	
01:30 P	99	75	10.6	
02:00 P	100	90	8.6	
02:30 P	100	96	4.7	
03:00 P	100	97	5.4	Continue stripping to meet VOC target.
04:00 P	104	100	1.6	
09:30 P	-	-	-	Stripping completed.

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[1] Approximate. From enthalpy calculations.

TABLE B-2. PROCESS DATA AT PLANT B
Aqueous Acetone Distillation

Initial batch charge	11,400L	3,000 gal.
Steam flow rate[1]	590-640 kg/hr	1,300-1,400 lb/hr
Process time (excluding 3.5 hr; batch on hold)		8.0 hr

Time	Batch (reboiler) Temp. °C	Column head Temp. °C	Reflux GPM	Product GPM	
04:30 A	20	-	-	-	Charged, started heatup.
05:00 A	26	-	-	-	
05:30 A	62	-	-	-	
06:00 A	70	57	-	-	Column head temperature lines out. Holding, total reflux.
07:00 A	70	56	-	-	
08:00 A	71	56	-	-	
09:00 A	72	58	7	-	
09:30 A	72	57	9	0	
09:35 A	-	-	-	-	Taking overhead product.
10:00 A	74	57	9	3	
10:10 A	-	-	-	6.5	
10:25 A	-	-	10.7	6	
10:30 A	74	58	10.7	6	
10:40 A	-	-	11	5	
11:00 A	74	56	11	2.5	
11:15 A	-	-	11	5	
11:45 A	75	56	11.2	4.5	
12:10 P	76	55	11.2	4.5	
12:25 P	79	55	11.2	4	
01:45 P	92	54	11.3	2.3	
02:30 P	98	56	11.5	6	
03:00 P	100	59	6	0	Steam cut back, product tank switch.
03:30 P	102	65	7	2	
03:45 P	102	66	7	1	

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[1] Approximate. From enthalpy calculations.

TABLE B-3. STEAM STRIPPER PROCESS DATA AT PLANT D
Batch 1 (Aqueous Xylene)

Initial Batch Charge	1,260 L	(334 gal)[1]
Final Batch Volume	1,420 L	(375 gal)
Organic (Xylene) Distillate	333 L	(88 gal)
Aqueous Distillate	248 L	(75 gal)
Steam Flow Rate	250-270 kg/hr	(550-600 lb/hr)[2]
Process Time	2.08 hr	

Time	Stripper Vapor Temp. °C (°F)	Distillate[3] Rate, L (gpm)	Steam Pressure kPa (psig)	Comments
04:15 p				Steam started to sparger
04:23 p	71 (160)		250 (36)	
04:35 p	68 (155)		264 (39)	
04:45 p	63 (146)		310 (45)	
04:48 p	68 (155)			
04:50 p	92 (197)		283 (41)	Distillate started over
04:55 p	93 (200)	9.5 (2.50)		
05:00 p		11.4 (3.01)		
05:45 p	97 (207)		303 (44)	
05:58 p	99 (211)			Final vapor temperature reached; stripping continued to reduce trace VOC
06:15 p	99 (211)			
06:20 p				Completed stripping

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[1] Measured volume in MST prior to transfer to stripper. Quantity of organic distillate indicates that approximately 200 L (60 gallons) of crude xylene may have been inadvertently charged to stripper.

[2] Calculated from heat of vaporization.

[3] Determined from incremental time-volume measurement.

TABLE B-4. PLANT D CONDENSER VENT FLOW READINGS
Batch 1 (Aqueous Xylene)

Time (p.m.)	Reading* (cu ft)	Rate (L/min)	Rate (cu ft/min)	Comment
4:00	38.058			Start filling
4:03	38.102	2.6	.091	Stripper
4:10:29	40.90	10.5	.370	
4:12:42	40.91	0.11	.004	Finish filling
4:16:13	40.92	0.08	.0028	Start steam
4:20:30	40.93	0.05	.0023	
4:24:30	40.94	.071	.0025	
4:25:24	40.95	.28	.01	
4:26:09	41.01	3.4	.12	
4:28:40	41.1	10.1	.36	
4:33:55	41.80	4.0	.14	
4:48:00	47.4	10.9	.386	
4:49:10	50.00	61	2.16	
4:51:00	56.0	84.9	3.0	Batch at temperature
4:52:00	57.3	36.8	1.3	
4:54:00	57.93	12.7	.45	
4:56:00	58.37	6.2	.22	
5:01:00	59.00	3.56	.126	
5:21:00**	59.66			
5:25:00	60.30	4.53	.16	
5:38:00	61.0	1.5	.054	
5:42:00	61.5	3.5	.125	
5:48:00	62.25	3.5	.125	

*Dry gas meter.

**Samples taken at 5:10, 5:14, 5:16, p.m. of vent gas.

TABLE B-5. STEAM STRIPPER PROCESS DATA AT PLANT D
Batch 2 (1,1,1-Trichloroethane/Oil)

Initial Batch Charge	895 L	(236.5 gal)
Final Batch Volume	323 L	(85.4 gal)
Organic (1,1,1-Trichloroethane) Distillate	670 L	(177 gal)
Aqueous Distillate	397 L	(105 gal)
Steam Flow Rate	250-295 kg/hr	(550-650 lb/hr)[1]
Process Time	1.72 hr	

Time	Stripper Vapor Temp °F	Distillate[2] Rate, L (gpm)	Steam Pressure kPa	(psig)	Comments
1249 p			262	(38)	Steam on to sparger
0103 p	149				
0108 p	150		234	(34)	
0115 p	152				
0124 p	157	21 (5.61)			
0135 p	205		269	(39)	
0145 p	208			(34)	
0151 p	210	5.1 (1.36)			
0155 p	211				Final vapor temperature reached; stripping continued to reduce trace VOC
0213 p	211		262	(38)	
0232 p					Stripping completed

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[1] Calculated from enthalpy of vaporization.

[2] Determined from incremental time-volume measurement.

TABLE B-6. PLANT D CONDENSER VENT FLOW READINGS
Batch 2 (1,1,1-Trichloroethane)

Time (p.m.)	Reading (cu ft)	Receiver Vent Rate L/min	Receiver Vent Rate cu ft/min	Comment
1:13	62.622			
1:17	62.83	1.5	10.052	
1:18:47	62.93	1.6	0.057	
1:20:03	63.03	2.5	0.087	
1:21:04	63.11	2.3	0.08	Negative flow start
1:23:06	61.70	-20	-.70	
1:25	63.10	+20	+.70	
1:36	64.4	3.4	0.12	
1:46+	64.8			Samples taken
1:56	66.1	3.7	0.13	
1:57:04	66.3	5.7	0.2	
1:57:38	66.4	11.3	0.4	
1:58:11	66.405	.28	0.01	
2:05	66.9	2.0	0.07	
2:06	67.1	5.7	0.20	
2:06:38	67.2	5.7	0.2	
2:07:07	67.3	5.7	0.2	
2:07:30	67.4	5.7	0.2	
2:08:25	67.5	2.8	0.1	

*Sampling of vent gas 49-3, 49-4.
**Negative flow, into process from air.

TABLE B-7. STEAM STRIPPER PROCESS DATA AT PLANT D
Batch 3 (Aqueous 1,1,1-Trichloroethane)

Initial Batch Charge	564 L	(149 gal)
Final Batch Volume	545 L	(144 gal)
Organic Distillate	45 L	(12 gal)
Aqueous Distillate	179 L	(47 gal)
Steam Flow Rate	272 kg/hr	(600 lb/hr)[1]
Process Time	0.93 hr	

Time	Stripper Vapor Temp. °C (°F)	Steam Pressure kPa	(psig)	Comments
0340 p				Steam on; started stripping
0345 p	68 (155)	262	(38)	
0402 p	97 (206)			
0414 p	98 (208)	262	(38)	
0428 p	99 (210)	276	(40)	
0436 p	99 (211)			Steam off; stripping completed

TABLE B-8. PROCESS DATA AT PLANT D
Batch 4 (Aqueous Mixed Solvent)

Initial Batch Charge	360 L	(95 gal)
Aqueous and Miscible Solvent Distillate	140 L	(37.1 gal)
Immiscible Distillate	3.2 L	(0.85 gal)
Steam Flow Rate	227-250 kg/hr	(500-550 lb/hr)[1]
Process Time	0.83 hr	

Time	Stripper Vapor Temp °F	Steam Pressure kPa	(psig)	Comments
0525 p		241	(35)	Started steam to sparger
0539 p	157			
0541 p	205	262	(38)	
0615 p	211			Stripping completed

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[1] Approximate. From enthalpy calculations.

TABLE B-9. SAMPLING TIMES FOR BATCH 1 (AQUEOUS XYLENE) AT PLANT D

Sample No.	Sample	Time	Comments
2500-45-4	Waste Feed Stream	0411 p	From stripper, prior to start of stripping
2500-45-3	Waste Feed Stream	0412 p	From stripper, prior to start of stripping
2500-45-5	Stripper Contents	0505 p	Approximately one-third through processing
2500-45-10	Aqueous Phase Distillate	0525 p	Mid process aqueous phase distillate
2500-45-6	Stripper Contents	0558 p	Approximately two-thirds through processing
2500-45-7	Stripper Contents	0620 p	Completion of stripping
2500-45-8	Aqueous Phase Distillate	0645 p	Batch aqueous distillate drummed off
2500-45-9	Organic Distillate	0650 p	Xylene product accumulated for batch, drummed off.

TABLE B-10. SAMPLING TIMES FOR BATCH 2 (1,1,1-TRICHLOROETHANE PRODUCTION) AT PLANT D

Sample No.	Sample	Time	Comments
2500-45-22	Waste Feed Stream	1248 p	Initial from stripper, prior to start of stripping
2500-45-23	Waste Feed Stream	1248 p	Initial from stripper, prior to start of stripping
2500-45-24	Stripper Contents	0128 p	Approximately one-third through process
2500-45-25	Stripper Contents	0155 p	Approximately two-thirds through process
2500-45-26	Stripper Contents	0232 p	Completion of stripping
2500-45-27	Miscible Solvent Tank	0310 p	Aqueous phase distillate accumulated for batch
2500-45-28	Product Storage Tank	0305 p	Organic product for batch

TABLE B-11. SAMPLING TIMES FOR BATCH 3 (AQUEOUS 1,1,1-TRICHLOROETHANE) AT PLANT D

Sample No.	Sample	Time	Comments
2500-45-29	Waste Feed Stream	0340 p	Initial from stripper, prior to start of stripping
2500-45-30	Waste Feed Stream	0340 p	Initial from stripper, prior to start of stripping
2500-45-31	Stripper Contents	0402 p	Approximately one-third through process
2500-45-32	Stripper Contents	0423 p	Approximately two-thirds through process
2500-45-33	Stripper Contents	0437 p	Completion of stripping
2500-45-34	Aqueous Phase Distillate	0440 p	Batch accumulation in decanter
2500-45-35	Organic Product	0441 p	Batch accumulation in decanter

TABLE B-12. SAMPLING TIMES FOR BATCH 4 (AQUEOUS MIXED SOLVENT) AT PLANT D

Sample No.	Sample	Time	Comments
2500-45-11	Waste Feed Stream	0523 p	Initial from stripper, prior to start of stripping
2500-45-12	Waste Feed Stream	0525 p	Initial from stripper, prior to start of stripping
2500-45-13	Distillate	0548 p	Condenser discharge
2500-45-18	Distillate	0548 p	Condenser discharge
2500-45-15	Stripper Contents	0552 p	Approximately one-third through process
2500-45-16	Stripper Contents	0601 p	Approximately two-thirds through process
2500-45-14	Distillate	0612 p	Condenser discharge
2500-45-19	Distillate	0612 p	Condenser discharge
2500-45-17	Stripper Contents	0615 p	Completion of stripping, final sample
2500-45-20	Aqueous Distillate	0630 p	From drum; distillate drummed from receiver
2500-45-21	Organic Distillate	0620 p	From drum; distillate drummed from receiver
2500-45-46	Plant Boiler Feed Water		Representative of live steam injected in stripper

TABLE B-13. GAS SAMPLES DURING STEAM STRIPPING AT PLANT D

Container number	Sample number	Time (p.m.)	Date	Description	Batch being processed
A88	2500-46-3	5:10	12/4/84	Product receiver	1
A181	2500-46-2	5:15	12/4/84	Product receiver	1
A160	2500-46-5	5:16	12/4/84	Product receiver	1
A175	2500-46-1	-	-	Field blank	
A100	2500-49-2	12:58	12/5/84	Product receiver	2
A79	2500-49-3	1:46	12/5/84	Product receiver	2
A104	2500-49-4	1:47	12/5/84	Product receiver	2
A84	2500-49-5	1:43	12/5/84	Product storage	2
A154	2500-49-7	1:15	12/5/84	Ambient air	
A173	2500-49-1	1:42	12/5/84	MST tank	2

APPENDIX C. ANALYTICAL PROCEDURES

The analyses that were carried out on the process samples are outlined below.

ONSITE ANALYSES AND MEASUREMENTS

The onsite analyses were limited to temperature measurement of the liquid samples. Temperature was measured immediately following sampling at each sample point. After collection of the 40-mL volatile organic analysis (VOA) bottle and 1-L samples, a glass jar was partially filled with a sample. The temperature was then measured using a mercury thermometer. The vent gas velocity was measured onsite using an Alnor velometer.

OFFSITE ANALYSES

Analysis of Vent Gas Samples

The evacuated stainless steel canister used to sample the vents was analyzed for volatile organics using the headspace GC method.

Analysis of Liquid Samples

Volatile Organics--
The volatile organic compounds in the liquid samples collected from the VOC removal processes were identified and quantified by both direct injection GC and headspace GC. Confirmation of GC peak identification was carried out by GC/MS on selected samples.

Determination of pH of Liquid Waste Samples--
The pH was measured using a pH electrode as described in EPA Method 150.1.

Determination of Solids Content of Liquid Waste Samples--
To characterize the waste material to determine the potential suitability of certain individual treatment techniques subject to solids limitations such as distillation and extraction, the total suspended matter and volatile and fixed matter in the waste material were determined. Standard Methods (Methods 209 C, D, E, and G) were used where applicable.

Determination of Density of Liquid Waste Samples--
A class A volumetric flask was filled and the weight of the liquid determined using an analytical balance.

APPENDIX D

QUALITY ASSURANCE

This appendix presents representative results of quality assurance data for the analysis of samples collected at Plants D and B. The relevant quality assurance for the grab samples taken on site visits (field blanks, duplicates) are presented with the data in the field test reports (Allen, 1985d, 1985g).

The general QA/QC project plan is presented in "Quality Assurance Plan: Hazardous Waste Pretreatment for Emissions Control," RTI, 1984, and the site-specific plans are described in "Site Specific Test and QA Project Plan Addendum Hazardous Waste Pretreatment for Emissions Control: Field Evaluation Plant D," RTI, 1984, and "Site-Specific Test and QA Project Plan Addendum Hazardous Waste Pretreatment for Emissions Control: Field Evaluation Plant B," RTI, 1984.

The analytical work was performed by Industrial Environmental Analysts, Inc. (IEA).

PRECISION, ACCURACY, AND COMPLETENESS

Clearly defined objectives for precision, accuracy, and completeness of the measurement data are necessary to ensure the generation of reliable data of known quality. This project has the analyzed waste samples for a variety of volatile organic compounds (VOC) from several pretreatment sites. Although a list of the specific VOCs expected could not be compiled before sampling because the types of wastes treated in the processes vary from day to day, the methodology that was selected to carry out the sampling and analyses was sufficient to characterize the processes to meet the program objectives.

The program's data quality objectives are given in Table D-1.

INTERNAL QUALITY CONTROL CHECKS

GC and GC/MS Analyses

A standard mixture of VOC in nitrogen is prepared in a large glass container. A sample of the standard gaseous mixture is withdrawn periodically to serve as the control for the GC headspace analyses. The gas sample from the standard is analyzed in an identical manner to the gas sample withdrawn from the headspace (see Page 190).

Liquid samples are analyzed by thermocouple detectors with gas chromatography for samples with high VOC concentrations (>0.1 percent) and by flame ionization detectors with gas chromatography for aqueous liquid samples

TABLE D-1. PRECISION, ACCURACY, AND COMPLETENESS OBJECTIVES

	Parameter	Units	Method	Precision % RSD	Accuracy (% Bias)[a]	Completeness[b] %
1.	Waste material flow rate	g/sec	mass flowmeter or calibrated container	10%	10%	100%
2.	Wind velocity	cm/sec	velometer	30	20	95%
3.	Source dimensions	cm	ruler	5	3	100%
4.	Gas temperature	°C	thermometer	5	1	100%
5.	Liquid temperature	°C	thermometer	5	1	100%
6.	Waste volume	m^3	dip stick	5	2	100%
7.	Gas flow rate	m^3/sec	calculated	10	10	100%
8.	pH of liquid	pH	EPA 150.1	±.1 units	± .1 units	100%
9.	Liquid density	g/m^3	gravimetric	1%	1%	100%
10.	Solids content of liquids	percent	209 C, D, E,[c] H as applicable	10	10	100%
11.	Water content of liquids	percent	ASTM, D-1744	20	10	100%
12.	Volatile organic compounds in vent gas	g/m^3	evacuated canister/ GC-FID	25	25	100%
13.	Volatile organic compounds in liquid samples	mg/L	GC-FID headspace GC-TCD direct analysis GC-MS	25 25 qual.	25 25 qual.	100% 100% 100%

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[a] percent bias = $\frac{\text{observed - expected}}{\text{expected}} \times 100\%$

[b] the number of valid data points divided by the number of planned data points expressed as a percentage.

[c] Standard Methods for the Examination of Water and Wastewater, 15th ed.

with lower concentrations of VOCs. The liquid sample was injected directly into the chromatograph.

GC/MS was used in a qualitative mode to verify the components identified by retention time by the gas chromatography. All reported compounds were verified by GC/MS.

SPECIFIC ROUTINE PROCEDURES USED TO ASSESS DATA PRECISION, ACCURACY, AND COMPLETENESS

For each major measurement parameter, the completeness, precision, and accuracy of the measurement data were evaluated. Completeness is a measure of the number of acceptable samples or data points actually obtained, divided by the number which were planned. Ways in which a sample can become "incomplete" or voided include not collecting the sample, sampling incorrectly, losing or breaking the sample in shipment, improper sample preservation, consuming the whole sample in a voided analysis, or outlier data point rejection. The completeness of the field tests was 100 percent.

Accuracy of volatile organic measurements is assessed on the basis of percent bias of analyses of performance evaluation samples. Percent bias is the difference between a measured value and the true value when the latter is known or assumed. Percent recovery describes either recovery of a known amount of analyte (spike) added to sample of known value, or recovery of an analyte of known value from a synthetic or environmental standard.

$$\%\ \text{Recovery}_{(\text{standard})} = 100 \times \frac{\text{observed value}}{\text{true value}}$$

Both percent bias and percent recovery were used to assess the accuracy of GC determinations.

Precision of volatile organic analyses was assessed on the basis of relative standard deviation of analyses of triplicate samples collected from each process. Relative standard deviation is calculated as follows:

$$\%\ \text{RSD} = \frac{S}{\overline{X}} \times 100\%$$

where S = standard deviation, and

$\overline{X}$ = mean of 3 or more measurements.

If only two samples are available for analysis, precision was calculated as relative percent difference as shown below:

$$\% \text{ RPD} = 2x \frac{X_1 - X_2}{X_1 + X_2} \times 100\%$$

where X_1 = first result, and

X_2 = second result.

Concentration values below the limit of detection of the methods employed result in the problem of determining how to report such values. This problem, when it occurred, was handled by reporting that the analysis was below the minimum detection limit and stating the minimum detection limit, such as <10 mg/L.

A measurement result will be considered an outlier whenever there is an obvious and documentable failure in the operation of the equipment or an obvious and documentable error committed by the analyst or operator. The measurement of the initial xylene concentration in the stripper as being much lower than the amount added to the waste water is an example of an obvious mixing error (or solubility problem). In addition, potential outliers in each data set can be tested using the method presented by F. E. Grubbs, Technometrics, 11(1), 1 (1969). The 95-percent level of confidence is used as the basis for acceptance or rejection.

PERFORMANCE AND SYSTEM AUDITS

Systems Audits

The RTI Quality Assurance Officer (RTI/QAO) performed a complete systems audit of the laboratories prior to field sampling. Additional audits were performed by S-Cubed, and the U.S. EPA.

Performance Audits

The RTI Quality Assurance Officer provided IEA with liquid samples to be analyzed as unknowns (the contents are described in Tables D-2 and D-3). Two of these samples were analyzed during the course of the project. The Quality Assurance Officer determined that acceptable levels of accuracy and precision were achieved based on program data quality objectives. The data quality objectives are reported in Table D-1, and the results of the audits are described below.

Results of Audit

Prior to the field sampling at Alternate Energy Resources, an audit sample was provided to IEA by the RTI/QAO. The sample consisting of several aromatic purgeable organics (xylene, toluene, benzene) at <1-percent concentrations was analyzed neat by GC/FID. The results were all within ±10 percent of the expected values. These results are presented in Table D-2. An additional audit sample was submitted for analysis containing a variety of chlorinated hydrocarbons. With the exception of methylene chloride (solvent

TABLE D-2. FIRST ACCURACY DETERMINATION OF VOC ANALYSIS

Compound	Concentration (mg/L) Expected	Concentration (mg/L) IEA	% Bias
Benzene	614	589	-4
Toluene	82	77.9	-5
Ethyl benzene	230	212	-8
p-xylene	382	351	-8
o- and m-xylene	1,064	984	-7

TABLE D-3. SECOND ACCURACY DETERMINATION OF VOC ANALYSIS

Parameter number	Parameter measured	EMSL certified values (mg/L)	IEA values (mg/L)	Percent bias
1	Methylene chloride	200	300	40[1]
2	1,1-Dichloroethene	104	110	5.6
3	Trans-1,2-dichloroethane	276	290	4.9
4	1,2-Dichloroethane	125	140	11.3
5	Carbon tetrachloride	133	140	5.1
6	1,2-Dichloropropane	200	180	-10.5
7	Trichloroethene	248	240	-3.3
8	Dibromochloromethane	148	130	-12.9
9	1,1,2,2-Tetrachloroethane	253	270	6.5
10	Chlorobenzene	202	200	-1.0

[1] The presence of methanol interfered with the analysis.

methanol interference) the concentrations which were determined were within the QA goals (25 percent). The results of the analysis of second audit samples is presented in Table D-3. The accuracy of the GC was checked regularly during the course of the analysis by injection of a gas reference sample containing toluene (100 ppm). An analysis of the results of 17 of these accuracy checks indicated a percent bias of +5.18 percent, with a standard deviation of 3.09 percent. These results are substantially better than the project goals of 25 percent.

Duplicate Analyses

Duplicate analyses were carried out regularly on headspace samples, liquid samples, and the gas samples collected in steel containers. In an analysis of 28 compounds from samples analyzed in duplicate, the average percent relative difference was 10.6 percent. The standard deviation on the distribution of these percent relative differences was 0.19, indicating that some of these duplicate analyses were less reproducible than others. The percent relative differences (Table D-1) for three samples were larger than the QA objectives (two samples of ethyl benzene and one of tetrachloroethene) near the detectability limit (3 x level of detection).

In the duplicate analyses of liquid samples (Table D-4), the precision was poorer than observed for the audit samples; however, this precision was still generally better than the quality goals of the project (25 percent) for the higher concentrations of interest (>1,000 ppm). The reproducibility (in terms of percent relative difference) is poorer for the components present at the lower concentrations.

In the duplicate analyses of gas samples taken in steel containers (Table D-5), the average percent relative difference was 23.8 percent, within the quality goals of the project (25 percent). Of the 17 comparisons, the percent relative difference was greater than 100 percent for one compound, in the range 15 to 60 percent on 6 compounds, and less than 15 percent on the remaining 10 samples of the distribution.

Linear Regressions

Linear regressions are used to evaluate the rate of stripping. The relationship between the logarithm of the concentration and the stripping time is linear for some of the VOC removal data. It is useful to estimate the error associated with the calculation of the slope. The least squares method is used to obtain the slope that minimizes the sum of the squares of the residuals.

The slope m and the intercept B are calculated by the following equation.

$$M = \frac{n\Sigma XY - (\Sigma X)\ (\Sigma Y)}{n(\Sigma X^2) - (\Sigma X)^2}$$

TABLE D-4. A COMPARISON OF RELATIVE DIFFERENCE FROM THE ANALYSIS OF LIQUID SAMPLES

Sample number	Compound	Analysis 1	Analysis 2	Relative difference
45-10	chloroform	83,000	86,000	0.035502
45-31	1,1,1-trichloroethane	71,000	100,000	0.339181
45-10	isopropanol	27,000	28,000	0.036363
45-10	1,1,1-trichloroethane	2,100	2,200	0.046511
45-10	acetone	1,000	1,100	0.095238
45-10	tetrachloroethane	260	250	0.039215
45-31	chloroform	250	34	1.521126
45-17	1,1,1-trichloroethane	230	230	0.000000
45-17	xylenes	120	4	1.870967
45-31	acetone	71	110	0.430939
45-31	xylenes	45	4	1.673469
45-17	toluene	35	3	1.684210
45-31	ethyl benzene	30	63	0.709677
45-10	xylenes	11	4	0.933333
45-31	isopropanol	6	14	0.800000
45-10	toluene	3	48	1.764705
45-31	toluene	3	8	0.909090

Total number of comparisons	17
Average relative difference	0.758
Standard deviation	0.6838

TABLE D-5. A COMPARISON OF RELATIVE DIFFERENCE FROM THE ANALYSIS OF GAS SAMPLES TAKEN IN STEEL CONTAINERS

Sample number	Compound	Concentration (mg/L) Analysis 1	Concentration (mg/L) Analysis 2	Relative difference
38	dibromoethane	550	300	0.588235
38	1,1,1-trichloroethane	530	330	0.465116
36	trichloroethene	350	310	0.121212
36	benzene	190	210	0.100000
36	tetrachloroethene	170	140	0.193548
36	methyl ethyl ketone	61	14	1.253333
36	isopropanol	52	50	0.039215
36	toluene	22	13	0.514285
204	methyl ethyl ketone	6.5	6.5	0 000000
203	1,1-dichloroethane	4.9	5.3	0.078431
203	methyl ethyl ketone	1.2	1.3	0.080000
204	methanol	0.98	1.2	0.201834
203	acetone	0.8	0.8	0.000000
204	isopropanol	0.58	0.62	0.066666
204	1,1-dichloroethane	0.49	0.52	0.059405
204	acetone	0.16	0.19	0.171428
203	carbon tetrachloride	0.16	0.18	0.117647

Number of comparisions	17
Average	0.238
Standard deviation	0.3069

$$B = \frac{\Sigma Y}{n} - M \frac{\Sigma X}{n}$$

where X is the stripping time, and Y is the natural logarithm of concentration, and n is the number of observations.

$$Sxx = \Sigma X^2 - (\Sigma X)^2/n$$

$$Syy = \Sigma Y^2 - (\Sigma Y)^2/n$$

$$Sxy = \Sigma XY - (\Sigma X)(\Sigma Y)/n$$

These standard error estimates can be used to calculate S^2 and r, which in turn can be used to calculate the confidence interval.

$$S^2 = (Syy - M\ Sxy)/(n-2)$$

$$r = Sxy/(Sxx\ Syy)^{0.5}$$

The confidence interval on M may be written as follows.

$$M \pm (t_{\alpha/2}S/(Sxx)^{0.5}$$

The students' t-distribution has n-2 degrees of freedom; the value depends upon the degrees of freedom.

The analysis of confidence limits for the calculated slopes are presented in Tables D-6 and D-7. In some cases the confidence limits could apparently have been substantially reduced by increasing the number of data points because of the sensitivity of t to the number of data points; in other cases, the relationship between the logarithm of concentration and time was not linear. This lack of linearity was particularly true for high concentrations of VOCs and for VOCs which were refluxed.

Other Procedures

The following procedures were carried out to ensure quality of the field evaluations:

- Both field and trip blanks were analyzed for the vent gas samples.
- One field blank was generated for the liquid samples collected at each site.
- One field replicate was obtained and analyzed for the vent gas sampling from each batch.
- All of the waste liquid samples were collected in duplicate.

TABLE D-6. CALCULATED CONFIDENCE INTERVALS FOR STRIPPING RATES AT PLANT D

Batch	Compound	Slope	Confidence interval (90%)	n
First Batch: aqueous xylene				
	acetone	0.0246	±0.096	3
	isopropanol	0.058	±0.0191	4
	methyl ethyl ketone	0.0393	±0.0056	4
	1,1,1-trichloroethane	0.0242	±0.0038	4
	xylene	0.0180	±0.0244	4
	tetrachloroethene	0.0296	±0.0140	4
Second Batch: production batch, 1,1,1-trichloroethane				
	1,1,1-trichloroethane	0.0648	±0.611	4
	methyl ethyl ketone	0.176	±0.096	3
Third Batch: 1,1,1-trichloroethane, MST	acetone	0.072[1]	±0.022	4
	1,1,1-trichloroethane	0.0468	±0.0073	4
	methyl ethyl ketone	0.0895[1]	±0.0193	3
	ethyl benzene	0.0208	±0.0140	4
Fourth Batch: mixed solvent				
	acetone	0.280	±0.147	3
	toluene	0.127	±0.120	4
	xylene	0.110	±0.050	4
	1,1,1-trichloroethane	0.0684	±0.019	4

[1] The first value less than detection limit included as the detection limit to reduce estimate of confidence interval.

TABLE D-7. CALCULATED CONFIDENCE INTERVALS FOR STRIPPING RATES AT PLANT B

Batch	Compound	Slope	Confidence interval (90%)	N
First Batch: acetone	acetone	0.0171	±0.0097	4
	isopropanol	0.0099	±0.00796	4
	methyl ethyl ketone	0.0172	±0.0141	4
	1,1,1-trichloroethane	0.0169	±0.0086	4
	toluene	0.0166	±0.0079	4
	ethyl benzene	0.0092	±0.0093	3
	xylenes	0.00937	±0.0076	4
Second Batch: MEK	2,2-DMO	0.0188	±0.0368	3
	isopropanol	0.0095	±0.0099	4
	methylene chloride	0.01889	±0.042	3
	methyl ethyl ketone	0.01718	±0.0635	3
	1,1,1-trichloroethane	0.000232	±0.00192	4
	methanol	0.00766	±0.0088	4
	trichloroethylene	0.00526	±0.00432	4
	benzene	0.00366	±0.00496	4

The GC/MS was calibrated with terfluorotributylamine. A standard series of 12 components were injected for a standard library search of compounds. These standards were verified each day that the GC/MS was used for liquid samples.

APPENDIX E

COST EFFECTIVENESS ESTIMATION METHODOLOGY

This appendix presents details of several components of the cost-effectiveness estimation methodology which was used (1) to derive unit treatment costs for the batches as processed in the field (Table 46) and (2) for analysis of how degree of waste treatment influenced unit treatment costs (Tables 47-50). The approach described below for handling condensate treatment was used in both these analyses. The other analytical details which are presented in this appendix support the analyses in Tables 47-50.

CONDENSATE TREATMENT

As the batch of waste is treated in the steam stripper, the condensed steam is collected in the MST; when the tank is full enough to constitute a batch, it is treated in the stripper. The stripping time is estimated for the treatment of this residual and included in the batch process time used in the cost estimates.

The amount of condensed steam is estimated as the product of the steam rate and the time that the steam is sparging. It is assumed that this condensate is treated for three time constants (reciprocal of the rate constant K) with the same ratio of steam to batch size as for the waste originally treated. The condensed steam is combined with condensed steam from other batches to form a 1,200 L batch for stripping. In addition to the condensate from the waste being treated, the condensate from the treatment of each condensate must also be treated. The dimensionless rate constant is assumed to be the same as for the original waste. The fraction of the condensate, F, that is generated from repeated condensate treatments that can be ascribed to an initial batch is theoretically an infinite series.

$$F = 1 + f + f^2 + f^3 + \dots f^n, \; n \rightarrow \infty,$$

$$f = \frac{\text{steam used to treat a batch}}{\text{batch size}} \frac{(L)}{(L)}$$

$$= \frac{3K^{-1}\ (\text{steam rate})}{\text{batch size}} \ .$$

The series solution of the fraction of steam treated is evaluated for the first eight terms. As f approaches 1, the series will become infinitely large. The waste treatment system may fail under these conditions; all that is accomplished by the treatment is that the volume of wastewater increases by condensed steam dilution.

The condensate treatment time is determined by multiplying the batch cycle time (three time constants plus 40 min) by the ratio of the wastewater volume (F x condensate) to the batch size (1,200 L).

BATCH CYCLE TIME AND BATCH PROCESS TIME

The batch cycle time is calculated from the first order decay equation using the average stripping rate constant, K, plus a batch heating and waste transfer time of 40 minutes. The stripping rate constants were determined from the logarithm of the ratio of the field values of the final VOC concentrations to the initial VOC concentrations, divided by the stripping times (as found in Table 27). Taking C(o) as the initial total VOC concentration for the batch and C(y) as the concentration of VOCs in the batch after y percent of the volatiles had been removed, then the batch cycle time required to obtain this percentage of removal, t(y), is:

$$t(y) = [K^{-1} \ln(C(0)/C(y))] + 40.$$

The batch process time is the sum of the times it takes to treat both the waste, t(y), and the condensate generated during the waste treatment (derived above).

OTHER PARAMETERS

Other parameters used in the cost analyses of Tables 47-50 are shown in Table E-1. The waste volume, rate constant for stripping, and the steam rate were assumed to be the same as for the batch evaluated during the field test. The maximum batch size for aqueous condensate treatment is assumed to be a typical batch size, 1,200 L. The product density and molecular weight is estimated on the basis of the composition of the major VOCs present.

Assumed costs for waste disposal at a landfill or at a publicly operated municipally treatment works (POTW) are provided, along with the assumed cost of steam.

The waste residual volatility (torr) is calculated on the basis of the sum of the concentrations (mg/L) of the VOCs measured in the headspace of the waste. This concentration is converted to a vapor pressure in the hypothetical case by dividing the ratio of this concentration of the VOCs in the vapor in the laboratory at 25°C to the concentration in the liquid in the laboratory and multiplying by the concentration in the hypothetical case, and multiplying by a factor of 0.0409 moles/L divided by the assumed molecular weight M (mg/mol), and multiplying by the vapor pressure of one atmosphere (760 torr).

TABLE E-1. PARAMETERS USED IN THE COST ANALYSIS

	Units	Batch 1	Batch 2	Batch 3	Batch 4
Waste volume		1,260	897	564	360
The rate constant for stripping, K	min^{-1}	0.073	0.06	0.048	0.132
The initial concentration	percent volatiles	26	74	18	3.1
The steam rate	L/min	4.33	4.53	4.53	4.00
The dimensionless rate constant	L-min./L/min.	21.23	11.87	5.97	11.88
Fraction VOC removal from condensate		95	95	95	95
Maximum condensate treatment batch size	L	1,200	1,200	1,200	1,200
Condensate treatment fraction	F	0.1646	1.3381	2.0013	1.3378
The product density	g/cc	0.86	1.33	1.33	0.95
Average VOC molecular weight		106	133	133	100
Waste disposal, landfill	$/L	0.37	0.37	0.37	0.37
Waste disposal, POTW	$/L	0.00005	0.00005	0.00005	0.00005
Cost of steam	$/L	0.0183	0.0183	0.0183	0.0183

APPENDIX F. SAMPLE CALCULATIONS

This appendix describes selected calculations performed for calculating various parameters and factors. Sample calculations for the field evalution at Plant A is provided in the first section. This is followed by cost-effectiveness calculations for a thin-film evaporator (Plant A) and calculations for the cost analysis of steam stripping.

EXAMPLE CALCULATIONS FOR THE FIELD EVALUATION AT PLANT A

Methylene chloride was present at 2.0 percent in the feed. The concentration in the product was 0.9 percent. There was no liquid analysis of the bottoms, but there was a headspace analysis of 0.03 mg/L. Assuming the same partition coefficient for the feed as for the bottoms, the estimated concentration in the bottoms was (0.03/1.7)(2.0 percent) or 0.04 percent. The following is a material balance assuming 95-percent product recovery of the feed, and assuming a 100-L feed basis. The methylene chloride lost from the vent is estimated by material balance.

Stream	Volume (%)	Percent methylene chloride by volume	Volume methylene chloride (L)
Feed	100	2	2
Product	95	0.9	0.86
Bottoms	5	0.035	0.0018
Vent	Unknown	Unknown	1.14

The percent removal of methylene chloride from the bottom sludge and associated liquids is (2 - 0.0018)/2 x 100, or 99.91 percent. The vent loss is (1.14 L/2.0 L) x 100, or 55 percent.

EXAMPLE CALCULATIONS FOR THIN-FILM EVAPORATOR UNIT OPERATING COSTS (Table 20)

At a feed rate of 23 L/min, the volume of waste treated is 23 x 60 x 24 x 273 or 9,040,000 L over a 273-day year, at 24 hours per day. Since the annual cost is $252,600, the cost per liter of waste treated is $252,600/9,040,000 L, or $0.0279/L. The cost of organic recovered (85 percent) equals ($0.0279/L waste) x (L waste/0.85 L organic) or $0.033. With a density of the organic of 0.8 Mg/m^3, the cost of recovering a metric ton of organic is $252,600/9,040 m^3/(0.85 m^{3}organic/m^3 waste/(0.8 Mg/m^3) or $41.10.

EXAMPLE CALCULATIONS FOR STEAM STRIPPING

The initial volume charged to the stripper in Batch 1 was 1,260 L. This contained 0.5 percent organics by weight or 7 L organics (density 0.866 g/cm^3). However, there were 333 L of organics recovered as condensate. Thus, there must have been at least 333 L of organics in the stripper initially (i.e., the stripper contained organics from a prior run). The initial water content is 1,260 - 7 or 1,253 L. This would imply an initial weight fraction of 0.866(333)/(0.866 x 333 + 1,253) or 0.187 (21 volume percent). The final batch volume is 1,420 L with nearly 500 mg/L or 0.0005 weight percent organics. Therefore, the percent VOC removed is [1 - 1,420 x 0.0005/(333 x 0.866)] x 100 or 99.8 percent.

Batch 1 has a volume of almost 1,590 L (1,253 + 333) and contained 21 volume percent volatiles. The steam rate was 4.33 L/min. The stripping rate constant is 0.073 min^{-1}. The batch cycle time is 40 min heating and transfer + 83 min stripping. The condensate is the steam rate x time or 83 min x 4.33 L/min or 359 L. The condensate treatment time is the prorated treatment time of a 1,600 L batch of condensate (3 time constants) x (13.7 min) x (359/1,600) + 40 min x (359/1,600) or 18.2 min. The volume of steam generated during this treatment was (41.1 min)(4.333 L/min)(1,600/1,590) or 179 L. The prorated amount to the treatment of the 359 L of wastewater was 359 x 179/1,600 or 40.2 L. Repeating the above process, the prorated condensate from treating the condensate's condensate would be 40.2 x 40.2/359 or 4.5 L. The treatment of the 4.5 L would be 4.5 x 40.2/359 or 0.504 L. The sum of these amounts of condensate treated is 359 + 40.2 + 4.5 + 0.504 or 404 L. The fraction F is 404/359 or 1.126.

The cost of the condensate treatment is the average cost of the waste treated ($262,900) divided by the annual volume (4,157,000 L) times the total condensate treated. 40.4 L divided by the volume of the batch (1,590 L), or $0.016/L waste. This cost of processing the condensate is adjusted by the solvent recovery costs ($0.20/L recovered VOC) x (0.8216 L VOC/L of waste). The recovery value is assumed to equal zero in this example.

The above cost of condensate treatment is not used in estimating the waste processing cost. The batch time is adjusted to accommodate the time for treating the condensate [123 min. + (18.2 min)(1.126)] or 143 min. The total operating time is 24 hours per day times 260 days or 374,400 min. At 143 min per batch, this is the equivalent of 2,617 batches or 4,157,000 L.